THE PHYSICAL, MECHANICAL, AND IRRADIATION BEHAVIOR OF NIOBIUM

AND NIOBIUM-BASE ALLOYS

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Introduction

The physical, mechanical and irradiation behavior of niobium and niobium base alloys have been widely studied over the last twenty-five years. Much of this interest stemmed from its favorable high-temperature strength and good low temperature ductility which prompted increasing emphasis on its use as a structural material in the aerospace industries in the **1960's**. Its strength characteristics combined with a low neutron absorption cross-section, also prompted its use in the nuclear industries.

Three "communities" have been active in the area to be covered by this review, with each group having its **own** specialized research interests. The first group has been concerned with the fundamental understanding of the various properties or processes occurring in niobium and the body centered cubic (b.c.c.) refractory metals in general, with research in this area being characterized by elegant experiments on ultra-high purity and doped single crystals. The second group has been interested in the high-temperature mechanical properties of niobium and niobium base alloys. The activity in the West, principally in the U.S.A., peaked during the 1960's (see, for Since the early 1970's the majority of the example references (1-16)). papers on these aspects have originated in the U.S.S.R. The third group has been concerned with the effects of irradiation in niobium and niobium base alloys. These studies were frequently prompted by the emergence of niobium as a candidate material for in-core components in specific nuclear reactor systems. For example, there has recently been considerable interest in the use of niobium and its alloys for structural applications in fusion reactor systems.

The activities of the first group have generally been reviewed under the property of interest. For example, Christian (17) has reviewed the low-temperature mechanical deformation mechanisms in the refractory metals, while Fisher (18) has reviewed the dependence of the single crystal elastic constants on electron/atom ratios. The primary aim of the present paper is to review the activities and data generated by the second and third groups. Thus, emphasis is placed on the physical and high temperature mechanical properties and effects of irradiation in polycrystaline niobium and niobium

base alloys. The review concentrates, wherever possible, on the data published since the last general reviews; see for example the reviews in reference (13). One of the main purposes is to highlight the strong influence which interstitial impurities have on both the mechanical and irradiation behavior of niobium and niobium base alloys. In support of this aim, the physical properties are reviewed with emphasis on the solubilities and mobilities of these impurities. The second main aim is to demonstrate the significant changes in properties, particularly mechanical properties, which are caused by alloying. The alloy systems which have been investigated are primarily those formed by niobium's near neighbors in the Periodic Table, (Table I). The Group Va and VIa elements, with the exception of chromium, are completely soluble in niobium. The Group IVa elements have high solubilities at elevated temperatures and furthermore react with the interstitial elements in the niobium to form second phase particles and thereby reduce the effective solubility of these elements, see the section "Physical Properties". Many binary, ternary and multicomponent alloys have been studied and advanced alloys developed for commercial applications. These will be detailed in the section 'Mechanical Properties of Niobium and Niobium Base Alloys".

Fable	I.	Niobium's	Near	Neighbors	i n	the	Periodic	Table

Group IVA	Group VA	Group VIA
$Ti_{22}^{47.9}$	v ^{50.9}	$Cr_{24}^{52.0}$
$2r_{39}^{22}$	NB40	²⁴ 95.9 Мо ₄₁
$Hf_{72}^{178.5}$	Ta ^{180.9} 73	w ^{183.9} 74

Physical Properties

There has been considerable interest in the physical properties of niobium and to a lesser extent niobium base alloys. In this review the data on the solubility of interstitial elements and the diffusion of both interstitial and substitutional elements will be highlighted as these are central to an understanding of the metallurgical and irradiation behavior of niobium and niobium base alloys. Prior to this, the main physical properties will be presented in "Physical Properties" for niobium and niobium base alloys.

Physical Properties of "Pure" Niobium

The principal atomic, thermal, electrical, magnetic and optical properties of pure niobium are given in Table II and III. They require little discussion here, features of note are the high melting point, (2468 C)the body centered cubic lattice and the electronic structure, $4d^4 \, 5s^1$. The latter implies that niobium has a valence electron/atom ratio (e/a) of five, which is particularly important in determining many of the bulk properties. The superconducting properties of niobium have been omitted as these are covered in other papers in the present conference proceedings.

The Principal Physical Properties of Niobium Base Alloys

Very limited data are available on the binary, ternary and advanced alloys of niobium which are the subject of this review. Available data compiled by Fountain & McKinsey for selected advanced alloys are given in Table IV (23). The data are incomplete and in some cases estimated on the basis of composition.

Atomic/Electronic/Mass/Crystal structure Α

Atomic weight Electronic configuration Density at 20 C Crystal structure = body centred cubic a = 0.3292	92.9064 4d ⁴ 5s ¹ .57 Ng/m ² nm
Thermal Properties	
Melting Point: Boiling Point:	2468± 10 C 4927 C
Linear Coefficient of thermal Expansion	
-6 -10 2	

 $\Delta \ell / = 6.892 \times 10^{-0} T \dagger 8.17 \times 10^{-10} T^2$ (T in K)

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Specific Heat	0.26 kJ/kg/K
Latent heat of fusion	290 K J/kg
Latent heat of vaporization	7490 KJ/kg
Thermal conductivity see Table 6	

С Electrical and Magnetic Properties

Electrical Conductivity at 18 C : 13.2% IACS Electrical Resistivity at 0 C 125 nΩ:m Temperature coefficient 0+600 C 0.395 ng;m er K Electrochemical Equivalent 0.19256 mg/C

Standard Electrode Potential $E^{O}(V) \text{ Nb/Nb}^{+5} 0.96$ Magnetic Susceptibility at 25 C 2.28 x 10 mks

Optical and Thermionic D

В

Refractive index 1.8 Spectral Emmissivity λ = 650mb = 0.37 Ionisation potential 6,67eV Work function 4,01eV

Table III,	Thermal	Conduct	tivity
C		₩/ш	K
0		52.3	
100)	54.4	
200		56.5	
300		58.5	
400	1	60.7	
500	1	63.2	
600)	65.3	

	Nbl Zr	Fs-82 (Nb-23Ta-1Zr)	Cb-65 Nb-8Ti-1Zr	Cb-74 Nb-10W-5Zr	D-31 Nb-10Ti-10Mo	F-48 Nb-15W-5Mo-1Zr	F-50 Nb-15W-5Mo-12r-1Ti
Melting Point (C)	2400 C	2510	2260 ^a	2430 ^a	2270	2480 ^a	2430 ^a
Density g/cm ³	8.66	10.2	8.06	8.98	8.08	9.4	9.1
Crystal Structure	b.c.c.	b.c.c.	þ.c.c.	b.c.c.	b.c.c.	b.c.c.	b.c.c.
Lattice Con- stant (nm)			0.3295		0.3229		
Thermal Conductivity Wm/K	41.8 (25 C)		22.2 (315 C)		71.1 (1200 C)	39.3 (25 C)	34.3 (25 C)
Linear coef. of thermal expansion			7.7 x 10 ⁻⁸ (25 - 120	6 0 C)	7.4 x 10 ⁻⁶ (0-1000 C)	8.8 x 10 ⁻⁶ (25-1150 C)	9 x 10 ⁻⁶ (25-1150 C)
Specific Heat kJ/kg/K	0.27 (25 C)		0.31 (25-1200 C))	0.31 (25-1200 C)		

	Table IV.	Physical	constants of	selected	semi-	-commercial alloys	(after	Fountain	and McKinsey	/ (23).
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estimated on the basis of composition.

Solubility of Interstitial Impurity Elements

<u>Pure niobium</u>. The solubilities of oxygen, nitrogen, carbon and hydrogen in niobium are given in Figure 1 (24-26). The first three increase with increasing temperature whereas that of hydrogen decreases. It is evident that very high concentrations of these elements may be dissolved at elevated temperatures, which should be contrasted with the very low solubilities of these interstitials in molybdenum, a neighboring element in the periodic table. This comparison illustrates how strongly the solubilities depend on the valence electron/atom, $({}^{e}/a)$, ratio; the typical solubility levels expected for different ${}^{e}/a$ ratios are given below: (14)

^e /a	wt ppm	
5.6 - 6	~ 0	(W, MO, Cr)
5	~ 1000	(Ta, Nb, V)
4	> 1000	(Hf, Zr, Ti)

Pionke and Davis (16), in discussing the equilibrium concentration – temperature relationships for the niobium-oxygen and niobium-nitride systems, made the important point that to prevent oxide formation $\underline{a}t$, say, 600 C, the partial pressure of oxygen would have to be kept below 10^{23} torr, while to prevent nitride formation $\underline{a}t$ the same temperature the nitrogen partial pressure has to be below 10^{5} torr. Further, for typical vacuum level of 10^{5} torr at 600 C the equilibrium oxygen concentration would be 600 wppm, which is more than sufficient to affect the mechanical properties of niobium. In general, \underline{as} will be discussed in the section "Mechanical Properties of Niobium and Niobium Base Alloys", the high solubilities of interstitial impurities in niobium are important in determining its response to applied loads; the properties are therefore particularly sensitive to the environment in which the tests are carried out.



INTERSTITIAL CONTENT - ATOMIC PERCENT

Figure 1. Solubility of interstitial elements in niobium as a function of temperature (Gases at Atmospheric Pressure) (24-26).

Solubility of Interstitial Elements in Niobium Base Alloys. The effect of the reactive Group IVa elements zirconium, hafnium and titanium has been most widely studied. Low levels of zirconium and hafnium have a strong influence on the solubility of oxygen and nitrogen in niobium base alloys. For example at 1000 C, \leq 1 weight percent zirconium reduces the oxygen solubility from 3800 wpm to 100 wpm (27) while a hafnium content of > 0.005atomic percent decreases the solubility of oxygen from 3-6 atomic percent to 0.25 atomic percent (28). Small additions of zirconium and hafnium also reduce the nitrogen solubility in niobium alloys but relatively high levels of these elements are required to produce a reduction in carbon solubility; in contrast titanium appears to have little effect on the solubility of carbon. At the usual zirconium, hafnium and titanium contents in the advanced alloys the solubility of carbon is quite large, and this has allowed the development of alloys, strengthened by distributions of carbides which are thus responsive to thermomechanical treatment.

Molybdenum and tungsten are the only Group VIA elements which have received attention in the literature. Additions of these elements do not markedly affect the solubility of carbon or oxygen, but they do reduce the solubility of nitrogen (29).

Diffusion

Self diffusion and impurity diffusion rates are important to many metallurgical properties, and as a consequence, there has been considerable interest **in** measuring self-diffusion and both substitutional and interstitial impurity diffusion in niobium; the results are summarized below.

<u>Self-diffusion and interstitial element diffusion</u>. Self-diffusion data for pure niobium are summarized in Table V, while Table VI includes diffusion data for interstitial elements. There is satisfactory agreement between the data obtained before 1978 for self-diffusion in niobium and the linearity of the Arrhenius plot covers more than ten orders of magnitude (30). However, Einziger et al (31) recently found evidence of non-linear Arrhenius behavior when studying the diffusion of ⁹⁵ niobium in niobium between 1353 and 2693K. This was interpreted **in** terms of a divacancy contribution.

The data given on oxygen diffusion are quoted from the work of Boratto and Reed-Hill (32, 33). It has to be noted that a controversey exists between these workers and McLellan (32, 33) as to whether the full, high and low temperature data for oxygen fits an Arrhenius plot. Boratto and Reed-Hill (32, 33, 37) believe that it does while McLellan disagrees (36).

There have been some studies of the effect of alloying on interstitial diffusivity. Perkins and Padgett (33) found that zirconium ($\leq 1 \text{ wt.}\%$) reduces the oxygen diffusivity (600-1100 C) through the formation of Zr-0 clusters. Lauf and Altsletter (38) also found that the oxygen diffusivity was reduced by alloying and estimated the following substitutional-oxygen binding or "trap" energies (eV) tantalum, 0.3 ± 0.1 ; vanadium, 0.55 ± 0.05 ; titanium, 0.7 ± 0.1 and zirconium 0.7 ± 0.05 and Vasileva and Voronova (39) found in niobium - 10 atomic percent (Mo or Ti and Zr) that the activation energy (kcal/mole) for nitrogen diffusion at 600 - 800 C was 21.2 in Nb, 22.1 - 22.3 in Nb+10 atomic percent molybdenum, 26.0 - 26.2 in Nb-10 atomic percent titanium and 32.5 - 32.7 in Nb-10 atomic percent Zr. These data indicate that zirconium has a strong influence on the diffusivity of both oxygen and nitrogen.

(m^2/s) <u>x 10⁴</u>	Q <u>kJ/mo1</u>	Temp Range
12.4	439.5	1535-2120
1.3	397.7	1680-2150
1,1	401.9	878-2400
3.8	421.1	1535-2120
0.85	393.8	878-2400
0.61	397.3	1150-2240

Table V. Diffusion data on pure niobium which fitted an Arrhenius Plot (30).

Table VI. Interstitial impurity diffusion in pure niobium.

	D_m ² /s	0 kJ/mol	Temp range	Reference
Oxygen	5.3 x 10 ⁻⁷	100.95	140-1000 C	32
	5.6×10^{-7}	100.96	140-1000 C	33
	3.78 x 10 ⁻⁷	106.3	550-1100 C	34
Nitrogen	2.6 x 10 ⁻⁶	152.3	270-1800 C	32
Hydrogen	1.6 x 10 ⁻⁴	7.7	190-310 K	35
Deuterium	5.94 x 10 ⁻⁵	12.8	233-310 К	35
Tritium	4.45	13.0	233-310 K	35

<u>Substitutional element diffusion</u>. Pelleg (30) has reviewed the substitutional alloy diffusion in niobium. The data compiled by Pelleg has been combined in Table VII with the more recent data of Albitzer (40, 41) to show the diffusion of these elements in niobium compared to niobium self-diffusion. It is interesting that molybdenum and tungsten have low diffusivity while vanadium, zirconium and titanium have high diffusivity. This has important implications concerning the effects on the creep behavior of niobium alloys.

Mechanical Properties of Niobium and Niobium Base Alloys

Introduction

Since the late **1950's** a great deal of effort has been devoted to the study of mechanical properties of niobium and niobium base alloys. In general, the coverage **is** very good particularly at elevated temperatures. However, certain topics, such as fatigue, seem to have been neglected.

∆Q <u>kJ/mol</u>	Q _{imp/Q_{Nb}}	^D imp/D _{Nb} (1545 C)
ті - 29.9	0.92	0.85
ті - 23.3	0.94	2.21
v - 38.0	0.90	32.20
v – 17.0	0.96	1.71
Cr - 44.3	0.89	6.61
Cr - 56.4	0.86	
Fe - 68.5	0.83	16.7
Fe - 99.5	0.75	12.1
Co - 136.6	0.75	40.4
Co - 119.2	0.70	42.3
Ni - 57.2	0.85	48.7
Ni - 129.6	0.67	565.0
v - 161.0	0.59	76.96
Zr - 29.6	0.92	3.9
мо + 116.9	1.30	0.046
Sn - 63.5	0.83	11.1
Ta + 21.9	1.06	0.27
W + 259.2	1.66	0.003

Table VII. Solute Diffusion from references (30, 40, 41).

 $\Delta Q = Q_{\text{solute}} Q_{\text{Nb}} : Q_{\text{Nb}} = 393.8 \text{ kJ/mole}$ $D_{\text{oNb}} = 0.85 \text{ x } 10^{-4} (\text{m}^2/\text{s})$

It is not intended to cover the low temperature deformation of single crystals of niobium $(\langle 0.2T_m \rangle)$ in this review. At these temperatures the strength increases rapidly as the temperature decreases (43) and the deformation processes are particularly complex (see for example 43-45). Numerous studies of these processes have been made in high-purity and doped single crystals and despite the considerable insight has been generated many fundamental questions remain unresolved. For example, the strong temperature dependence on the yield stress and flow stress in this region has been attributed to either the interaction between the residual interstitial content and the dislocations present (46, 47) or to an intrinsic property of dislocations in the bec structure (48).

The range of alloying elements that have been used to strengthen niobium has already been covered in the section "Physical Properties". The two main strengthening mechanisms involved are solid solution strengthening and second phase particle strengthening. The most potent solid solution strengtheners are the Group VIA and VA elements W, Mo and V which are completely soluble in niobium. The group IVA elements (Ti, Zr and Hf) at low concentrations (< 2-3 wt.%) are regarded as dispersion strengtheners because of their interaction with interstitial elements which results in the formation of oxides etc. At higher concentrations part of their effect may come from a solid solution strengthening mechanism. Precipitation strengthening has also been achieved by increasing the interstitial impurity content to give an alloy containing a high volume fraction of dispersed particles. In niobium, NbC, NbO, and NbN are normally precipitated **as** large particles both within the grains and at grain boundaries, and give very little strengthening. A suitable distribution of finely divided precipitates can be achieved by adding reactive elements to alloys having increased interstitial contents. This has been most successfully demonstrated with carbon additions since the solubilities of oxygen and nitrogen are dramatically reduced by the reactive element additions and it is extremely difficult to obtain an optimum distribution of oxides or nitrides. Carbon retains a high solubility at elevated temperatures and alloys responsive to thermo-mechanical treatments have been developed.

It is beyond the scope of this review to include all the data that has accumulated over the last three decades. In presenting the behavior of "pure" niobium, the important effect of the interstitial impurities will be stressed. In describing the alloy data, the aim will be to illustrate the significant property changes introduced by alloying by reference to selected binary, ternary and advanced alloy systems of niobium. A more thorough description of the properties of the many binary, multi-component and advanced alloy systems that have been studied may be found in references (1-15). It is appropriate to review the compositions of the niobium and niobium base alloys that have been included in these investigations.

Composition of Niobium and Niobium Base Alloys

It was indicated in the introduction that the mechanical properties of niobium are strongly influenced by its purity. As the purity is determined by the method of production, it is important to establish the various routes by which niobium may be prepared and to give the typical levels of residual impurities which are achieved by each process. In the early 1960's there were three main methods for consolidation; powder-metallurgy, arc-melting, and electron-beam melting. Typical analyses are given in Table VIII; the final purity depends on the purity of the starting material but it is evident that the greatest degree of purification and ultimate final purity is obtained by electron-beam melting. A review of these consolidation processes has been presented by Pochon (19). Ultra-high purity material produced by zone melting has been used on a laboratory scale to prepare small-single crystals and Schulze et al (20) have given an excellent discussion of this production process.

A very wide range of alloy systems has been studied including the binary and ternary alloys comprised of elements in Table I and a number of complex allovs that have been developed for commercial or semicommercial applications. Table IX summarizes the compositions of the most advanced alloys developed in the West, in the mid to late 1960's (21). Following Frank (21), they have been classified as high, medium and low strength. The high strength alloys usually have tungsten or tungsten and molybdenum levels in excess of 20 wt. percent while the medium strength alloys have lower levels of these elements. The major constituents of the low strength alloys are the Group IVa elements (Ti, Zr and Hf). Pionke and Davis, (16) in their excellent assessment of niobium base alloys for fusion reactor applications, gave Nb-1Zr, Cl03, SCb 291, C129Y and FS-85 as being commercially available in 1978: of these C103 was considered to be the most widely used high-temperature niobium-base alloy. Table X lists the alloy systems of commercial and semicommercial availability in the USSR (circa 1977) taken from Morgunova (23). Also included are alloys labelled "development" to which there are frequent references in the Russian literature (1970 - 1980). A surprising feature is that only one of the alloys contains tungsten while the rare earths lanthanum and cerium are a feature of the VN series. No detailed information on the applications of these alloys **is** available; it may be significant that since 1970 the majority of references to the VN series are concerned with various aspects of their welding and brazing.

Deformation, Recovery and Recrystallization

The mechanical properties of niobium and niobium base alloys are influenced by the initial thermo-mechanical treatments. For example, niobium strain hardens at a low rate and thus the pure metal can be cold-worked with large reductions in thickness without the necessity of intermediate annealing. This section discusses the formation and thermal stability of the deformation induced substructures which give rise to this behavior.

Table VIII. Typical Purity of Niobium Achieved by Different Consolidation Technique								
<u>Route (19)</u>					<u>Purity</u>			
		<u>0</u>	$\frac{N}{2}$	<u>C</u>	<u>H</u>	Fe	Ti	Ta
Powder Metallurgy	(a) (b)	0.5 0.05	0.07 0.01	0.25 <0.01	ND	0.05 0 .05	0.05 0.05	0.3 0.3
Arc-Melted	(a) (b)	0.08 0.05	0.03 0.024	0.023 0.021	0.0029 0.0014	ND ND	ND ND	ND ND
Electron- beam	(a) (b)	0.16 0.004	0.022 0.006	0.03 0.009	0.0016 <0.001	<0.001	<0.001	0.069
(a) Sta	rting	materia	al (b)	Purifie	ed Material	ND	Not detern	nined

	Table LX	, Com	positic (West	on of Ad Circa	vanced 1968)	Nb-base	e Alloys	3
<u>High</u> Strength	Ā	Mo	.Ta	<u>T1</u>	Zr	<u>v</u>	Hf	Other
Cb-1 B-88 VAM 79 Cb-132M AS-30 F-48 Sp-31	30 28 22 15 20 15	5	20		1 2.5 1 1		2 2	0.06C 0.06C 0.13C 0.1C 0.05/0.1C
Moderate Strer and Ductility	ngth						3.5	
Su-16 FS-85 D-43 Cb-752 SCb-291 C-129Y B-66 AS-55 PWC-11 PWC-33	11 10 10 10 10 5	3	28 10		1 1 2.5 1 1 1 3		2 10 5	0.08C 0.1C 0.2Y 0.2Y 0.1C 0.35C
Low Strength and High Ducti	lity							
Cb-753 C-103 B-33 D-14 D-36 ≬b-1Zr				1 10	1.25 0.7 5 5 1	5	10	
Table X.	Composi	ition o <u>N</u> b-b	f Comme ase All	ercial S loys : U	Semi-Cor JSSR (19	mmercia 177)	al and De	evelopment
Commercial and Semi-Commercia	al <u>W</u>	Mo	<u>Ta</u> 1	<u>Li Zr</u>	<u>v</u> <u>H</u>	f		Other
VN2 VN4 VN2A VN5A RN6	4.5-6	3.2-5.2 3,5 - 10, 3.5-4.7 5-7 4.5-6	5	1-2 0.5-0 0.5-0 1-1.5	.9 .95	€0, 0.0 0.0 0,0	05C 1-0.05 8C, 0.01 8-0.15C	La, Ce 0.25–0.4 15–0.04 La, Ce
IRMNI) IRMN2) NO IRMN3)	composit.	ion ava	ilable					
Development								
Nb-l2r-0,lC A-44 SVMTS SVMTSU SVTTS	5 4.9 4.5	2.2 2.0	2.0	1 4.25 0.7 0.2 3.5		0.1 0.3	C 5N	

Substructure formation

<u>"Pure" niobium</u>. The development of the dislocation substructure at room temperature in polycrystalline niobium **has** been studied by several authors (49, 50, 51). Representative results were obtained by Thompson and Flewitt (49). Working with niobium wires and strip having an initial given size of 90 microns and containing < 50 ppm oxygen and a total interstitial impurity of < 115 ppm. The dislocation arrangements formed in cold-rolled strip on increasing deformation are summarized in Table XI. The most significant aspect of these observations was the development of a cell structure at > 20 percent deformation and the small change in cell structure as the level of deformation on straining in tension although they observed cell development at slightly lower strains (8%). It is thought that the cell boundary is not a strong obstacle to the propagation of slip dislocations (53), and this is clearly an important factor in the development of the cell structure.

The work of Van Thorne and Thomas (51) demonstrated that the development of this cellular substructure is important in determining the mechanical response of niobium. They found that a cellular network formed only in impure material containing precipitates and that this material work hardened with the flow stress dependent on the square root of the dislocation density. Cells did not develop in pure material which as a result did not work harden to the same extent and exhibited a flow stress with a lower dependency on dislocation density. These results also highlight the important role which interstitial elements play in substructure formation.

after formig at form temperature				
Deformation	Dislocation Arrangement			
Undeformed	3×10^6 lines cm ⁻² - some sub-boundaries			
5%	7×10^{-8} lines cm ⁻² - fairly uniform distribu- tion both $a_{12}^{(11)}$ and $a^{(100)}$ burgers vector observed			
10%	-10^9 lines cm^{-2} - in localized areas small clusters of dislocations formed			
>20%	Dislocations form a cellular structure within individual cells dislocation density is low 10 ⁶ lïnes cm ² . Cell size 0.4 x 0.4 x 0.05µ			
80%	Cell walls thicker and contain more disloca- tions. No change of dislocation density within individual cells. Cell size $-0.4 \times 0.4 \times 0.01\%$			
98%	Cell size decreased and individual cells less easily distinguished as they contained tangles of dislocations.			

Table XI. Dislocation arrangements formed in niobium after rolling at room temperature

From Thompson and Flewitt (51)

Substructure formed in Nb alloys. There is very little information on the substructure produced by deformation in niobium alloys. Cellular structures are formed in Nb-lW-lZr (134) strained 10 percent in tension indicating little difference from the behavior of niobium strained in tension (see 50). In Nb-lZr 0.1 wt. percent C, Glazunov (54) found that a cellular structure was formed after 30 percent cold rolling; the development of the substructure at higher levels of deformation similar to that found by Flewitt and Thompson (51) in cold-rolled pure niobium. However, the yield strength and <u>true</u> strength were independent of deformation, indicating that the cell walls were, **as** in niobium (53), still weak barriers to slip.

Recovery

The thermal stability of the deformation structure is of vital importance in the retention of strengthening imparted by prior thermal-mechanical treatments. In heavily deformed material the dislocation cell structure is not stable at elevated temperatures; the stored energy of cold work being reduced by recovery and primary recrystallization processes. The studies on recovery are confined to pure niobium and will be reviewed below.

In heavily deformed niobium (95% cold rolling) Foatedar and Monteiro (55) observed no change in the average cell size after one hour anneals at 25-400 C. Above this temperature, the cell/subgrain size increased linearly up to 680 C after which the subgrain size tended to saturate. Minakov et al (56) studied the growth kinetics of deformation cells in niobium (deformed by 90%) in the temperature range 500 - 900 C, and found that the cells grew at a constant rate, with an activation energy of 28.1 kJ/mol. This is much lower than the activation energy for self or grain boundary diffusion, recrystallization and polygonization. The authors noted that the value was similar to the activation energy for interstitial atom migration. They considered that cell growth would continue as long as interstitial atoms were created inside the cell boundary by the motion of dislocations. As these diminished in density the cell wall would become more like a polygonal wall or grain boundary, which would require a much higher activation energy for motion (145-500 kJ/mol).

Recrystallization

<u>Recrystallization in "Pure" niobium.</u> In general the recrystallization of niobium follows the expected classical pattern. It is controlled by the composition, degree and temperature of cold work, annealing time and most importantly annealing temperature. This can be seen from the results of Page (57), on arc-cast material, and Begley and France (58), on electron-beam melted material, presented in Figures 2 and 3 and Table XIII. The interstitial content of the material is given in Table XII. Begley and France (58), found lower recrystallization temperatures (965-1160 C) than Page (1130 -1250 C) for the same degree of cold-work and annealing time, (see Table XIII). This may be linked to the lower levels of interstitial impurities in the electron beam melted material. Begley and France (57) also studied isothermal grain growth of their electron-beam melted material between 1000 and 1200 C. There was a slight increase in grain size at 1200 C but little change at 1000 and 1100 C. No information was found which referred explicitly to secondary recrystallization.



Figure 2. Approximate beginning and end of recrystallization; prior deformation indicated on curves (57).



Figure 3. Approximate beginning and end of recrystallization deformation indicated on curves (58).

Recrystallization of niobium alloys. The recrystallization data on the alloys are mainly concerned with the effect of binary additions. The combined data of Savitskii (59) and Bartlett (60) are presented in Figure 4. The higher recrystallization temperatures of pure niobium reported in the Russian work may be attributed to the influence of impurity elements carbon, oxygen and nitrogen. Both sets of data confirm that tungsten and molybdenum raise the recrystallization temperature. Interesting features of the results of Savitskii et al (59) are that microalloying has a very pronounced effect on the recrystallization temperature and that some elements may depress the recrystallization temperature, i.e. B, Cr, La; while V and Ti initially increase and then decrease the recrystallization temperature.

Second phase particles also affect the recrystallization behavior. Data on recrystallization temperatures T_R in Nb-Zr alloys are given in Table XIV (61, 62). The higher values of T_R in the Nb-Zr-C system after 80 percent deformation may indicate that the carbides present in this alloy stabilize the cell structure at high levels of deformation.

There have been few systematic studies reported in the literature on the recrystallization behavior of multi-component alloys as a function of cold work, grain size and annealing temperature. However, the indications are that the general pattern given above is followed. For example, Pionke and Davis (16) quote data on Cb-65 (Nb-7Ti-0.82r) and F-50 (Nb-5Mo-15W-5Ti-12r-0.06C). After 75 percent reduction, the Cb-65 alloy had the same recrystallization temperature as Nb-12r, but the molybdenum and tungsten additions and second phase particles in F50 raised the recrystallization temperature and the alloy required one hour at 1760 C for complete recrystallization even after 85 percent reduction.

The above discussion is concerned with primary recrystallization. There are little data on secondary recrystallization in niobium alloys. Bankoviskii et al (63) report that in Nb-Zr-N alloys the stable nitride particles inhibited secondary recrystallization until 1700 C; substantial grain growth occurred above this temperature following coalescence of the nitride phase.

Fracture Mechanisms and Ductile-Brittle Schavior

Fracture Mechanisms

Fracture - mechanism map of "pure" niobium. The fracture map for niobium derived from published data by Gandhi and Ashby (64) is shown in Figure 5. This diagram, with tensile stress as one axis and homologous temperature as the other shows the fields of dominanace of seven mechanisms of fracture by which a crystalline solid loaded in tension might be expected to fail. The fracture mechanisms and the construction of the maps are discussed by Ashby et al (65) and Ashby (66).

Niobium shows the expected pattern of fracture behavior for many bcc metals, the most dominant feature of which is the range of stress and temperatures at which brittle behavior is encountered. Below about (0.07 T_) = 70 C

niobium fails by cleavage on {001} and also {110} planes with negligible ductility. This occurs either through the propagation of pre-existing cracks at flaws or more usually mechanical twinning or slip cracks which propagate either by cleavage or along grain boundaries. As the temperature increases the flow stress falls and extensive plasticity precedes fracture; higher stresses are required to initiate cracks and measurable ductility precedes cleavage fracture. The extent of this field depends on grain size and interstitial impurity. As the temperature increases, a gradual transition to ductile fracture occurs.

Table XII.	Interstitial co	ontent o	of niobium em	ployed	in		
recrystallization studies							
		C	٩	N	(wt	bbæ)	
Page (57)	Arc-cast	300	500	360			
	Powder Metallurgy	200	900	300			
Begley (58) and France	Electron- beam melted	190	250	200			

Table XIII. Recrystallization temperatures* and activation energies for recrystallization

		<u>Recrystallization</u>		
		temp	°C	
	Activation			
Reduction	Energy	Begley and		
%	(kJ/mol)	France (57)	Page (58)	
50	-	-	1250	
60	682	1160		
80	640	1070	1171	
95	624	965		
97.5	-	-	1130	

* Defined as the temperature at which recrystallization was complete after a 1 hour anneal.

Table	e XIV.	Recrystallization i	n Nb-12r Allo	oys
<u>1-98</u>	%Zr (6	1)	<u>Nb-1%Zr-0</u>	1%C (62)
CW	T _R *		CW	т _к
20% 80%	1400 1000	C C	10% 80 C	1450 C 1200 C

 T_{R} = recrystallization temperature



Figure 4(a). Data of Bartlett et al (60).



Figure 4(b). Data of Savitskii et al (59).

Figure 4. Effect of alloying elements on the recrystallization temperature of niobium and its alloys.



Figure 5. Fracture Map for Niobium (64).

At above 0.3 $\, {\rm T}_{\!_{\rm T}}$ niobium starts to creep and at high stress transgranular

creep fracture occurs. The intergranular creep fracture is depicted by Gandhi and Ashby at low stresses because no fractographic information is presently available. The authors state that the rupture field is included by analogy with maps for other bcc metals.

<u>Fracture mechanisms in Nb alloys</u>. Most of the interest in the fracture behavior of the niobium alloys has centered on the ductile-brittle transition temperature and possible embrittlement rather than on the fracture mechanisms over a wide temperature range. However, it is to be noted that the second phase particles that are frequently a feature of the advanced alloys may exert a considerable influence on the fracture mechanisms. The most complete study of this is the work of Ban'kovskii et al (67) on the fracture under a tension deformation rate of $10^3/\text{sec}$ of the alloy NTsAV8 which contains 4 percent by volume of ZrN. The authors were able to identify the role of the low strength ZrN particles in controlling the fracture mechanisms observed at test temperatures between -196 and 1550 C.

Ductile-Brittle Behavior

<u>Ductile-Brittle behavior in "Pure" niobium</u>. In common with all bcc metals, niobium exhibits a ductile to brittle transition at low temperatures, with the ductile to brittle transition temperature (DBTT) depending on both the metallurgical state of the material and the testing method. Niobium exhibits good tensile ductility down to -200 C. This can be seen from the work of Begley and Platte (69) who demonstrated that the smooth bar transition temperature of four purities of niobium was always between -190 and -196 C. Similarly, Wessel, France and Begley (68) only obtained brittle transignature at temperatures of about -215 C.

The transition temperatures given by the more severe impact tests are generally higher for impure niobium. This is illustrated in Figure 6, which concerns data of Begley and Platte (69) and Minchin and Sheeley (70) for electron-beam melted and arc-cast material. The relevant impurity levels are given in Table XV. Both sets of data gave a similar transition temperature of -200 C for the electron beam melted material. The transition temperature of the arc cast material was close to 0°C in both cases, although the exact temperature determined in the two studies was different. Begley and Platte also observed that the transition temperature of the arc-cast material was relatively insensitive to prior deformation as the DBTT was only lowered slightly when the material was tested in the cold-worked rather than the recrystallized condition. The major effect of the deformation was to reduce the impact strength (shelf energy) above the transition temperature.

Grain size has also been shown to influence the DBTT. From tension tests Churchman (71) reported that cleavage fracture occurred at -195 C in coarse grained niobium (+ 0.4% oxygen) but not in fine grained material. Wessel and Lauthers (72) found a strong dependence on grain size in commercial Nb - 0.6 Zr, rolled and recrystallized and tested in tension. Their results are given in Table XVI.

<u>Ductile-Brittle behavior in niobium alloys</u>. The effect of selected binary additions on the DBTT is illustrated in Figure 7. The majority of elements raise the DBTT, with the exception of titanium and hafnium which cause little change. The pattern of behavior resembles the effect of alloying additions on the recrystallization temperature, with Mo and W having the greatest effect.



Figure 6. Effect of temperature on impact properties of electron beam and arc-cast niobium. Curves 1-3 are from Charpy V-notch test pieces of electron beam melted (curve) and arc-cast material (curves 2 and 3) (69). Curves 4-6 are from modified Izod test pieces of electron beam melted material (curve 4), arc-cast (curve 5) and arc-cast and cold worked material (curve 6). See Table XV for impurity levels.



Figure 7. Effect of binary additions on the temperature for 10 percent reduction in area (73).

Material	Test	c	wt. percent	N	Condition	Ref.	Figure 6
8+	Charpy	0.021	0.010	0.009	Recrystallized	70	1
A*	v-not ch	0.030	0.040	0.020	Recrystallized	70	2
A*		0.03	0.040	0.070	Recrystallized	70	3
8+	Mod	0.020	0.014	0.030	Recrystallized	69	4
A*	Type	0.025	0.027	0.014	Recrystallized	69	5
A*		0.025	0.027	0.014	Cold-worked	69	6

 $E = \text{electron-beam melted } A^* = \text{Arc-cast material}$

Table XVI.	Transition Temperature for Nb + 0.65	Zr, Rolled
	and Recrystallized Sheet (72).	

Transition Temperature
-175 -150
-150 -100

For the advanced alloy systems, Frank (21) quotes Westinghouse data on the bend transition temperature for a series of medium strength alloys, B-66, C129Y, Cb 752, D43, D43Y, FS-85, and SCb-291. With the exception of D43 the alloys exhibited good low temperature ductility. The transition temperature for D43 ranged from -100 C to 24 C depending on prior thermomechanical treatment.

An important aspect of the ductile-brittle behavior of the alloys is the question of whether or not the DBTT is affected by long-term ageing at elevated temperatures. Stephens (74) found that ageing C-103 and Nb-lZr for 1000 hours at temperatures between 700 and 1025 C had no significant effect on the DBTT, but that ageing Cb-752 at 900 C raised the DBTT from -196 to -150 C. The author suggested that a critical combination of W and Zr levels in this alloy led to Zr segregation at grain boundaries which resulted in the observed embrittlement.

Effect of interstitials of the ductile-brittle behavior. The DBTT of both niobium and niobium base alloys is usually raised by the presence of interstitial impurities. The data presented in Figure 8 demonstrates that both oxygen and nitrogen can raise the DBTT of niobium to above $0^{\circ}C$. Nitrogen appears to have a greater embrittling effect than either carbon or nitrogen (75). Hydrogen has also been observed to severely embrittle niobium (76) tested in tension and this is discussed in the section below.

For niobium base alloys, the limited data available confirm that interstitial impurities raise the DBTT. Table XVII summarizes the results of Mahoney and Patton (77) on the effect of increased oxygen, nitrogen, and hydrogen levels on the DBTT of Cb-752 and of Stephens (74) on the DBTT of Cb-752, C-103, and Nb-12t. Both sets of results demonstrate that the DBTT of Cb-752 is particularly sensitive to interstitial levels. In constrast, the transition temperature for C-103 was relatively insensitive to hydrogen levels. Whereas the DBTT of Nb-12t was increased only when hydrogen was added after ageing treatments.

Slow Strain-rate dependent embrittlement of niobium. Niobium in common with the other Group Va metals is subject to slow strain-rate embrittlement when interstitial elements are present at levels below the solubility limit. The niobium-hydrogen system has been the most widely studied. Tensile testing of niobium-hydrogen alloys at < 0°C generally indicates a ductilebrittle-ductile transition (79-82), although a simple ductile-brittle transition has also been observed (82-85). Any ductility minimum observed is dependent on both the strain rate and hydrogen level, Figure 9. The embrittlement has been attributed to either hydrogen in solution or to precipitated hydrides. Recently other authors (86) have shown that the embrittlement is caused by the stress-induced formation of hydrides in advance of the crack tip. The brittle hydride cleaves along [110] and the crack front advances; the step-wise precipitation and cracking of the hydrides formed in front of the crack allows the rapid propagation of the crack. This hydride mechanism is controlled by hydrogen diffusion to the crack tip and Gahr et al (86) demonstrated that the inverse strain rate effect and the return to dutility at low temperatures can be accounted for by the limited growth of hydrides.

Birnbaum (87) has discussed the applicability of this mechanism to the brittle fracture resulting from the presence of other phases (oxides, ni-trides, carbides, helium bubbles, etc.). From the general requirements which must be satisfied for this mechanism to lead to brittle fracture he has derived expressions for the upper and lower temperature bounds T_{r_i} and T_{r_i}

respectively for this phenomenon and applied these to various systems including Nb-0 and Nb-N. The values of T and T for Nb-0 and Nb-N are given in Table XVIII.

Donso and Reed-Hill (88) found that slow-strain rate embrittlement occurred in niobium containing > 0.5 at percent oxygen in the temperature range 325 C - 725 C which is below the solubility limit for oxygen at the test temperature. By analogy with hydrogen embrittlement a ductile-brittle-ductile fracture transition was observed; the ductility decreasing with decreasing strain-rate and increasing oxygen concentration.

Tensile properties

The elevated temperature tensile properties of niobium and niobium base alloys have been very widely studied. In "pure" niobium the important effect of interstitial impurities has been identified as well as the influence of other metallurgical and test parameters such as strain rate and grain size. The strengthening effect of a wide range of alloying elements and second phase particles have been studied, and the tensile properties of the advanced alloys are well established. Interstitial elements can be picked up from the testing environment and since this can have a marked effect on the tensile

properties only data obtained in an inert atmosphere or a vacuum of < 10^{-5} torr will be presented in this review.



Figure 8. The effect of interstitial impurities (C,0,N) on the bend test transition temperatures (75).



Figure 9. Reduction in area vs. temperature for several recrystallized Nb-H alloys (79). Button-head tensile specimens of ~ 0.15 in. diameter and 0.75 in. guage length tested at 77 K, 191 K and 300 K in a floor-model Instron testing machine.

Heat Treatment	Imp	ourity (wpp	(m	DBTT C	Ref.
	<u>0</u>	N	Ħ		
1 hr. vacuum anneal at 1100 or 1200 C	250-330 620-830 630-860 860-1390 890-1420	150-250 500-675 >670 >670 >630	10-75 18-85 80-110 ≻180 ≻210	-196 - 80 25 100 200	77 77 77 77 77 77
Annealed 1 hr. 1345 C and Aged for 725 C	126	100	37* 37*	50 65	74 74
1000 hr. at 825 C 900 C 975 C 1025 C			39* 38* 40 * 41*	70 100 80 80	74 74 74 74

Table XVII A. Effect of Changes in Oxygen, Nitrogen and Hydrogen levels on the DBIT of Cb 752.

* Hydrogen introduced at 850 C (10 min) after heat treatment.

Alloy and heat	treatment	Impuri	<u>ty (wppm)</u>		DBIT
C-103					
Annealed 1 hr. Aged for 1000 hrs. at	1345 C 725 825 900 975 1025	130	40	74 72 69 61 53 39	< -196 C
<u>Nb-12r</u> Annealed 1 hr. Aged for 1000 hrs. at	1345 C 700 825 925 975 1025	73	70	51 53 59 55 58 28	<-196 C -100 C

Table XVII B. DBTT of Hydrogen-Doped Alloys, C-103, and Nb-12r (74).

* Hydrogen introduced at 850 C at a pressure of 10 mm after annealing treatment.

Table XVIII.	Upper, T , and	d Lower Ten	nperatures,	T,, fo	r
	embrittling	to occur (8	37)	Ľ	_
	Embrittling	Tu		т _L	
System	Phase	<u>(°K)</u>		(°K)	
			10 ^{-5*}	10 ^{-7*}	10 ^{-9*}
Nb-0	NЪO	1220	890	685	555
Nb-N	NЪ ₂ N	1100	1170	900	725

Moduli of elasticity

<u>"Pure" niobium</u>. Reported values of Young's modulus, E, for polycrystalline niobium at room temperature tabulated by Tietz and Wilson (10) in 1966 vary between aproximately 100 and 125 GPa, suggesting that the modulus may be sensitive to the method of preparation, purity and test conditions. More recently Gschneider (89) reported a value of 105 ± 0.7 GPa and Wreidt and Oriani (90), a value of $E = 100.1 \pm 1.3$ (GPa).

Brown and Armstrong (91) and Armstrong and Brown (92) studied the temperature dependence of the Young's Modulus, E, and found that cold-worked specimens and samples annealed below 1000 C showed a slow decrease of E with increasing temperature (curve 1 Figure 10) while samples annealed for 1 hr at 1800 C exhibited an increase in E between 200 C and and 1050 C (Curve 2, Figure 10). This behavior was attributed to the strong [110] recrystallization texture in the latter specimens; studies of single crystals revealed that E decreases with increasing temperature for [100] orientations but increases for [110] and [111] orientations. For further discussion of single crystal elastic constants see Talmor et al (1977) (93) and for a general review of the elastic moduli of bcc transition metals see Fisher (94).

<u>Niobium alloys</u>. Harris (95) determined the Youngs Modulus, E, between 80 and 373 K using a static method in tension for a range of binary alloys, Nb-Ta, Nb-V, Nb-Zr (250 ppm interstitial impurities) and Nb-W with 100 wt ppm interstitial impurities. At -296 K the increase in E with concentration was roughly linear in all the alloys for concentrations greater than - 34 at percent. At small concentrations, there were deviations from this linearity. V and Ta caused small deviations downward while W and Zr gave deviations upward.

Yield Strength, ultimate tensile strength and elongation measured at elevated temperatures

"Pure" niobium. The elevated temperature tensile properties of recrystallized commercial niobium (69) arc melted (70) and electron beam melted materials (70) are shown in Figures 11 to 13. The impurity levels are given in Table XIX. The most notable feature of the temperature dependence of the ultimate tensile strength and yield strength is the loss of strength at temperatures above 400-600 C due to the onset of recovery and recrystallization processes. This is particularly clear in the case of the electronbeam melted material, The less pure materials exhibit a higher strength at temperatures below the onset of recovery and recrystallization as can be seen from a comparison arc-melted or commercial niobium with electron beam melted This reflects the important effect which the interstitial elements material. have in raising the strength in this temperature range. The interstitial elements present in the less pure materials also give rise to the dynamic strain ageing peaks at 300 C. The effect of interstitial impurities is further discussed in the following section "Effect of interstitial impurities".



Figure 10. Modulus of elasticity of niobium vs. test temperature (91, 92).



Figure 11. Effect of temperature on the ultimate tensile strength of recrystallized commercial niobium (curve 1) arc melted (curve 2) and electronbeam melted niobium (curve 3) (69, 70). Details of the impurity levels and test parameters are given in Table 19.



Figure 12. Effect of temperature on the yield strength of niobium. See caption of Figure 11 for details.



Figure 13. Effect of temperature on the elongation of niobium. See caption of Figure 11 for details.

	<u>Test</u> Pa	Interstitial Impurity			^r Curve in	
	Specimen	<u>Strain rate</u>	<u>C</u>	<u>0</u>	N	Figure
Recrystallized commercial Nb (69)	1/4 in. diam	1 x 10 ⁻³ per sec	0.024	0.019	0.019	1
Electron-beam melted (70)	0.178 in. diam. by 1 in gauge length	0.005 per set to yield strength then 0.05 to failure	0.021	0.010	0.009	3
Arc-melted (70)	0.178 in. diam. by 1 in gauge length	0.005 per sec to yield strength then 0.05 to failure	0.027	0.040	0.010	2

Table XIX. Impurity levels of materials considered in Figures 11-13.

<u>Niobium base alloys</u>. There have been many studies of the strengthening effect of binary additions to niobium. The additional strength provided by the Group IVA, VA, VIA elements is presented in Figure 14 for a test temperature of 1095 C. It can be seen that all of the elements studied with the exception of titanium and tantalum gave considerable strengthening. It has also been found that molybdenum and tungsten strengthen without causing a marked loss of ductility, and that a significant minimum in ductility occurre(at 5 percent zirconium. Fountain and McKinsey (23) noted excessive scatter in the data at room temperature, suggesting that differences in purity and metallurgical history are important at this temperature. The effect of ternary and quaternary additions may be seen from the data on Nb-SV given in Table XX (23). All alloy additions produce additional strengthening, although zirconium additions cause a marked loss of ductility.

The second phase particles formed by the reactive metal additions also provide additional strengthening. This is illustrated in Figure 15 where the ultimate tensile strengths of three niobium-zirconium alloys are compared with the strength of niobium (curve 1). It can be seen from curve 4 for carbide strengthened and curve 5 for nitride strengthened material that the dispersed carbides and nitrides gave rise to higher strength than either Nb-1 Zr (curve 2) or pure niobium (curve 1). However, comparison of curves 3 and 4, both for the carbide strengthened alloy FWC 11, highlights the necessity of following the optimum thermo-mechanical treatment. In the <code>dioblug-zircoa-ium</code> system the optimum volume fractions of both nitrides and carbides have been found to be 3-4 percent (99, 100) with the carbide strengthened alloy giving slightly greater strength below 1200 C.

In the Nb-Hf system, second phase particles formed by interstitial element additions give considerable strengthening, although in this case the results of Grigovitch et al (101) suggest that at room temperature and 1200 C, nitrides give greater strength than either carbides or oxides.

As might be expected, different yield strengths are obtained when dispersion strengthened alloys are tested in tension and compression. Ban'kovskii et al (63) studied a Nb-8W-Zr-N alloy with 4 vol percent ZrN and found that at 600-1000 C lower yield strengths were obtained in tension; this was attributed to particle-matrix interface fracture. The ratio of the yield strengths tested in compression and tension decreased from 1.27 at 600 C to 1.06 at 1000 C.



ALLOYING ELEMENT (ot 2)

Figure 14. Relative strengthening effect at 1095 C for recrystallized binary niobium alloys (23).



Figure 15. Effect of temperature on the ultimate tensile strength of the following alloys:

Curve 1	Pure niobium
Curve 2	Nb-l percent Zr
Curve 3	PWC 11 (Nb-1Zr-0.1C) Recrystallized at 1400 C
	(1 hr) and aged 1 hr at 900 C.
Curve 4	PWC 11 hot extruded (9:1) at 1675 C and rolled
	into rod ($\epsilon \sim 30\%$) at 1427 C.
Curve 5	NTSA-44 Recrystallized for 1 hr at 1600 C

	<u></u>	10,5 (IIC	Jiii 101. 20 /	<u>. </u>				
		Roo	1095 C					
Alloying Additions	Heat Treatment	.02% <u>Y.S.</u> (a)	<u>U.T.S.</u> (b)	Elonga- tion_	0.2% <u>Y.S.</u>	<u>U.T.S.</u>	Elonga- tion	
5V-5Mo	Annealed 1600 C	77.2	95.0	28.7 27.3		40.1	43.5	
5V-5Mo-1Zr	1 hr.	-	-	-	50.5	53.5	5.0	
5V-5Mo-12r	Stress Relieved 1 hr. at 1095 C	83.0	101.3	34.9	42.4	47.4	41.8	
5V-7.5W	Annealed 1600 C	89.0	125.8	21.9	41.0	43.2	30.7	
5V-5W-1Zr	1 hr.	84.6	104.5	32.4	46.5	50.5	18.6	
5V		74	82	28	33	37	38	

Table XX. Tensile properties of tenary and quaternary alloys (from ref. 23).

(a) Y.S. = Yield Strength

(b) U.T.S. = Ultimate tensile strength

The ultimate tensile strength, yield strength and ductility for selected high strengh, Su 31, medium strength FS85, Scb 291 and low stength Nb-12r advanced alloys, (102-105) are plotted in Figures 16-18. It is evident that solid solution, dispersion and precipitate strengthening are only effective up to 1400-1600 C and that high strength at lower temperatures is achieved at the expense of ductility. It is interesting that all the zirconium containing alloys show maxima in their UTS at 500-900 C. This is suggestive of dynamic strain ageing.

<u>Effect of interstitial impurities.</u> Interstitial elements in solution strongly influence the elevated temperature tensile properties of niobium and niobium base alloys. Yield point phenomena, solution hardening, and dynamic strain ageing are observed in niobium and in niobium alloys containing significant levels of interstitial impurities.

The pronounced yield point phenomenon exhibited by niobium (and other refractory metals) when tested at low temperatures is thought to occur through the locking of dislocations by the segregation of impurities. When the dislocations are freed from the pinning atmosphere the yield point is surmounted and the applied stress decreases. Blanter et al (97) estimated that the binding energy between interstitial impurity atoms and dislocations in niobium was $.32 \pm .03$ (eV) for oxygen and $.15 \pm .05$ (eV) for nitrogen.

In the case of pure niobium, Szkopiak (109) and Elsner and Horz (110) have demonstrated that nitrogen was a more effective solution hardener than oxygen by a factor of 16 to 1.8. In addition, Szkopiak (111) has shown that the flow stress increased linearly with increasing oxygen and nitrogen content and that the solution hardening coefficients were strain rate independent but vary, with plastic strain; nitrogen again being twice as effective as oxygen.



Figure 16. Effect of temperature on the ultimate tensile strength of Su 31, FS 85, SCb 291 and Nb-1Zr (102-105).



Figure 17. Effect of temperature on the yield strength of Su 31, FS 85, SCb 291 and Nb-1Zr (102-105).



Figure 18. Effect of temperature on the elongation of Su-31, FS 85, SCb 291 and Nb-12r (102-105).

The reduction of the solubilities of the interstitial impurities in alloys containing reactive elements, such as zirconium, limits the possible solution hardening. This is probably the reason why increasing the oxygen, nitrogen and hydrogen levels in Cb-752 had little effect on the strength at room temperature (77). Obviously, if the impurity levels are increased to such an extent that precipitates are formed, then strengthening will result. This is illustrated by the work of Lakhtin et al (113) who demonstrated that nitriding 1mm sheets of VN2AE (Nb-4.7Mo-.52r-.02C) and VNB (Nb-4.7 Mo-1.6Zr-.15C) at temperatures between 900 and 1200 C increased the UTS at room temperature by 50-100 percent, probably through the formation of dispersed nitride precipitates.

Dynamic strain ageing peaks are a feature of both niobium and niobium alloys (particularly those containing Ti, Zr and Hf). The different interstitial impurities cause different dynamic strain ageing temperatures. This is most clearly illustrated by the work of Amonenko et al (106) concerning the temperature dependence of the UTS of niobium containing different combined levels of oxygen, nitrogen and carbon. Their results are shown in Figure 19. A high level of nitrogen caused a peak at 450-600 C (curve 2), while a high level of oxygen caused a peak at 200 - 350 C (curve 3). These peaks were not observed in the high purity material (curve 1), although, in common with the other materials, a small peak was observed in the neighborhood of 400 C. This has been attributed to the action of carbon. The serrated shapes of the load deformation curves and reduced ductility in the regions of the peaks confirm dynamic strain ageing. These dynamic strain ageing temperatures are in agreement with the earlier work of Dyson et al (107) and Minchin and Sheeley (70). As might be expected, the magnitudes of these peaks are sensitive to strain-rate, and disappear at high strain rates (78).

In the alloys, Wilcox and Allen (96) observed that the addition of 25 percent zirconium to Nb-10 W causes the dynamic strain ageing temperature to shift from 200-500 C to 650-1000 C ($\epsilon^{\circ} = 1.7 \times 10^{-3}$). They concluded that the results were not explicable in terms of the effect of zirconium on the

mobility of oxygen and they tentatively suggested that the inhibition of recovery by precipitation played an important part in the observed shift.

<u>Effect of grain size</u>. The dependence of the lower yield stress a on the grain size, d, was originally represented by Hall (114) and Petch (115) for alpha iron as:

 $\sigma = \sigma_1 + k_y d^{-1/2}$ (1)

 σ_1 represents the frictional stress and k_y is a measure of the contribution to the stress made by the grain boundaries. This relationship has been found to hold for niobium but there has been considerable variation in the values of k_y reported (0-1.7 kg/mm^{1/2}). Szkopiak (116) concluded that this was due to oxygen or nitrogen pick-up during annealing, since he observed a k_y value of 1.7kg/mm^{3/2} in strain annealed samples which did not show changes in interstitial content, while annealed specimens in which pick-up occurred gave a lower k_y of 0.8kg/mm^{3/2}. The value of k for cells (0.16Kg/mm) is considerably lower than the value for grains (53), implying that a cell boundary is not as strong an obstacle to the propagation of slip as a grain boundary.

The limited data available in the alloys suggests that the Hall-Petch relationship **is** obeyed provided second phase particles are not formed **on** grain boundaries (141).

<u>Strain hardening and strain rate sensitivity</u>. Body centered cubic metals have a low strain hardening rate at all temperatures (98). Strain hardening coefficients for niobium calculated from true stress – true strain curves at room temperature are 0.2 to 0.25 ($_{\sigma} = K_{\varepsilon}^{n}$ where n is the strain hardening coefficient). The strain hardening coefficient also tends to decrease with increased amounts of strain; in cold-rolled niobium (80-90% reduction) the strain hardening coefficient is 0.05.

The strain rate sensitivity, m, defined as

is observed to increase slightly with grain size and has a value of between 0.88 and 0.11 for vacuum purified material tested at room temperature (228). A somewhat lower value (.03) was determined by Mincher and Sheely for the lower yield stress of arc-cast material (70).

Creep and Creep-Rupture

Creep Strength

<u>Creep strength of "Pure" niobium</u>. The creep behavior of niobium follows that of other pure refractory metals; primary, secondary and tertiary creep are observed, the presence and extent of each stage being determined by the temperature and stress levels. The stress and temperature dependence of creep deformation for Group VA metals niobium and tantalum, taken from Begley et al (117) is shown in Figure 20. The 100 hour stress rupture tests tend to



Figure 19. Effect of temperature on the ultimate tensile strength of niobium containing different combined levels of oxygen, oxygen, nitrogen and carbon (106). Test pieces with 22 mm guage length and 5 x 0-5 mm² cross-section were tested at a strain rate of 1.6 x 10⁻³ Sec⁻¹ in a vacuum of 5 x 10⁻⁵ torr. Curve 1 5 x 10⁻³0, 3 x 10⁻³N, 10⁻²C (wt %) Curve 2 6 x 10⁻³0, 7.5 x 10⁻³N, 10⁻²C (wt %) Curve 3 5 x 10⁻²0, 5 x 10⁻³N, 10⁻²C (wt %)



Figure 20. Summary of high temperature deformation of the Group VA refractory metals (melted material only) (117).

have several percent primary creep, a steady-state creep rate of $= 10^{-6}$ sec⁻¹, and a third or more of the test life in the tertiary stage of creep. Creep ductility is high (> 50%); there is litte evidence for void formation or intercrystalline cracking and creep fracture is transcrystalline. With the very low creep rates (~ 10^{-9} sec⁻¹ for 1%strain in 1000 hrs.) there is little if any primary creep.

The stress dependence of steady-state creep has generally been expressed as a power function.

$$\sigma = \varepsilon^{n} (\sigma = \text{stress}, \varepsilon = \text{strain rate})$$
(3)

with values of n between.4 and 7 (105) although Barmore et al (110) reported a value of 9.3 in tests between 700 and 1000 C.

 $\frac{Creep strength of niobium alloys.}{the elastic modulus and lower the atomic mobility have been found to be effective creep strengtheners of niobium.} For example tungsten and molybdenum are particularly effective at >0.5T in accord with their slow$

diffusion rates in niobium (see section "Physical Properties"). However, the data in the literature on specific alloying elements are difficult to correlate (118-123). This is probably due to differences in experimental technique and test parameters.

The general creep strengthening behavior of binary and ternary additions is best illustrated by the work of Klein and Metcalf (123), who studied the creep strengthening due to additions of rhenium and the elements in groups IVa - VIa, with the exception of titanium, at temperatures between .4 and .8T,. They employed an abbreviated test method in which creep testing was conducted at high temperature in a vacuum of 10^{-7} to 10^{-8} torr and the stress adjusted to give a steady-state creep rate of 10⁻⁵ per second. The temperature was then lowered and the procedure repeated until the entire stresstemperature profile had been obtained. The results demonstrated that all the solutes studied increased the creep strength but that they were frequently most effective in particular composition and temperature ranges. Zirconium and hafnium were most effective at low concentrations and temperatures, while the solid solution strengtheners tungsten and molybdenum contributed most at high temperatures and concentrations. Vanadium, which McAdam (122) found to lower the creep strength, strengthened more at low rather than high concentrations but there was no strong dependence on concentration. Tantalum was only effective at concentrations of greater than ten atomic percent. In a subsequent paper they established that the creep strength of ternary alloys was frequently higher than the binary data would have predicted. This points to the importance of solute interactions in determining the creep strength of multicomponent alloys.

Distributions of finely divided second phase particles have been shown to be effective creep strengtheners. The creep strengths of alloys containing the optimum volume fraction of zirconium carbide (100) or zirconium nitride (101) or hafnium nitride (63) are comparable at 1100-1200 C with those of alloys containing high levels of tungsten and molybdenum. There have been relatively few direct comparisons of the creep strengthening achieved by the different second phase particles, although McAdam (122) considered that HfC gave slightly better creep strength at 1200 C than the same volume fraction of 2rC or TiC.

A further aspect of creep strengthening by second phase particles is the thermal stability of the precipitate distribution. Changes in the precipitate distributions frequently occur after prolonged ageing at elevated temperatures, and this may affect the creep strength. This is illustrated by the work of Kissil et al (137) who found that ageing the alloy 5VMT's for 5000 hours at 900 C cause an increase in precipitate density which was thought to account for the increase in creep strength at 1100 C observed after the alloy had been aged. In contrast, the change in carbide morphology during ageing of the Nb-1 Zr-0.1 C for up to 10,000 hours at 900 C (136). The authors suggested that the decrease in interstitial content in solution in the aged material would decrease the extent of dislocation dissociation and make cross-slip easier; this would lead to a decrease in creep strength at this temperature.

The stress rupture properties of selected high strength, (Cb-1, Su31) moderate strength, (FS-85 and Cb-752), and low strength, (Nb-12r), advanced alloys are given in Figure 22 on the basis of stress as a function of the Larson-Miller parameter, (21). The pre-test conditions are set out in Table XXI. The creep strengths of these alloys are generally in accord with the data on binary alloys, 1.e. those alloys with high levels of tungsten exhibit good stress rupture properties. This is particularly well illustrated by the increase observed on going from Nb-12r to FS-85 which contains a further 10 percent tungsten.

Table	XXI. I	Pretest	Treatmen	ts	(See I	Figure	22	for s	tres	s
	rup	oture p	roperties	of	these	e alloy	s).			_
	съі	(a)	1732	С		1 hr				
	сы	(Ъ)	1371	С		1 hr				
	Su 3	31 ^(c)	1600	С		1 hr				
			+1200	c		3 hr	s.			
	Fs 8	35 ^(d)	1472	С		1 hr				
	Cb 7	752 ^(e)	1538	С		1 hr	+	40% C	W	
			+1316	С		1 hr				
	Cb 2	752 ^(f)	+1205	С		10 #	in			
	Nb-1	lZr ^(g)	1700	С		1 hr				
	Ub-1	Zr ^(h)	1600	С		1 hr	+	1200	С 3	hrs.

All the alloys considered in Figure 21 are wholly or partially strengthened by second phase particles and they all exhibit some sensitivity to pretest heat treatments. As indicated above, this may partly be due to the different distributions of second phase particles produced. A further contributing factor may be differences in the grain-size distributions produced by different annealing temperatures. Tsviluk et al (135) considered the large grain size produced by annealing the alloy 5VTTs at 1700 C to be an important factor in the increase in the 100 hr. stress-rupture strength at 1100 C compared with specimens annealed at 1400 C. Futher, Vasil'eva and Trekina (142) considered that changes in the grain boundary structure during pre-test treatments might also contribute to creep strengthening of niobium alloys.


Figure 21. Stress-rupture properties of selected niobium base alloys; high strength Cb-1, Su-31, moderate strength FS 85 and Cb-752, and low strength Nb-12r (21).



Figure 22. Measured activation energy, Qc, for the creep in niobium determined in studies (125-131). The value of the self-diffusion energy Q is indicated on the vertical axis of the figure.

<u>Measured activation energy for creep</u>. A frequently measured parameter in creep studies is the activation energy for creep, which defines the temperature dependence of the creep rate. Its importance lies in the fact that its magnitude frequently allows the rate-controlling creep mechanism to be determined. The measured activation energy for creep is usually defined as

$$Q_{c} = kT^{2} (\partial \ln t^{1} / \partial T)_{\sigma Z}$$
(4)

where $\varepsilon^{\mathbf{1}}$ is the creep rate, T is the temperature and the stress σ and structure z are held constant. The true activation energy for creep can be expressed in terms of Q and a correction for the variation in elastic modulus with temperature.

In pure niobium there have been several measurements of Q (125-131). At temperatures below .45T_m Q_c has been found to be less than the activation energy for self diffusion Q_{sd} . This has been taken to indicate that creep is controlled by processes such as cross-slip, pipe diffusion, or grain boundary diffusion. Above $0.5T_m Q$ is close to Q_{sd} which is consistent with diffusion controlled creep processes. However, considerable scatter is observed, which may, as indicated in Figure 22, be attributed to differences in test method, strain rate etc. Klein and Gulden (129) postulated that the high values given in their test of the material labelled A in Figure 22 was caused by dynamic strain ageing involving substitutional atom impurities. The authors further suggested that the structural instabilities resulting from this strain ageing may have contributed to the scatter in the values of Q_c reported by other workers.

The limited information available on the effect of alloying suggests that alloying modifies Q_c . Lazerer and Ugaste (130) demonstrated that in the temperature range 1100-1400 C, molybdenum additions increase the measured value of Q_{\bullet} In the Nb-Zr system it was observed that at 1040-1300 C the addition of up to 1 percent Zr caused Q to increase but that further additions resulted in a reduction. These results are illustrated in Figure 23.



Figure 23. The effect of molybdenum (130) and zirconium (131) additions on the measured activation energy for creep in the temperature range ~ 1100-1400 C.

Influence of interstitial impurities on creep. In pure niobium both oxygen and carbon have been observed to give creep strengthening, and this has been interpreted as arising through the clustering of the interstitial elements. For example in the studies of Rawson and Argent (128) it was found that the presence of up to 600 ppm carbon, which produced carbides, led to decreased creep rates. The authors also observed that up to 1200 ppm of oxygen decreased the creep rate at below 1050 C but had little influence on creep properties at higher temperatures. The authors suggested that the strengthening was due to oxygen clusters which were not thermally stable at above 1050 C. In contrast, Stoop and Shahinian (127) considered that up to 3500 ppm of oxygen produced an order of magnitude strengthening in both the minimum creep rate and rupture times in the temperature range 0.55-0.62T_w.

Relatively little direct information was found on the effect of interstitial impurities on the creep behavior of niobum **alloys**. However, many authors have observed that test vacuum has an effect on the creep behavior. This is clear indication that interstitial element pick-up during the test has an important effect. In alloys containing reactive elements, the creep strength is usually decreased when the vacuum is improved (132).

Fatigue

Relatively little fatigue data are available for niobium. Enrietto Sinclair and Wert (108) studied niobium containing different levels of oxygen, (0.001%, 0.02%, 0.43%). At temperatures below 500 C, the fatigue limit increased with oxygen content and the fatigue limit at 10^7 cycles for the three oxygen contents shown in Figure 24.

Chung and Stoloff (138) found that hydrogen had a significant effect on the room temperature fatigue behavior of niobium under both low frequency strain control and high frequency stress control test conditions. In the latter, hydrogen had a beneficial influence on the fatigue life but in low frequency tests increasing hydrogen decreased the fatigue life. The authors also observed that crack initiation occupied most of the fatigue life of hydrogenated niobium and that estimated crack growth rates were increased significantly when hydrogen was present.



Figure 24. Fatigue limit of niobium vs. test temperature for various oxygen contents (108).

There have been few studies of the fatigue of niobium alloys. Begley (139), using flexural tests found that in Nb-1 Zr alloy, the endurance limit of 0.050 mm sheet at 10^{-7} cycles was 172 and 200 MPa for cold-worked materials and 193 and 214 MPa for annealed material. Tension - tension tests of annealed 0.1 cm sheet of the alloy D31 (Nb-10Ta-10Ti) indicated that an endurance limit of 10^6 cycles would be 400 MPa at room temperature and 92 MPa at 1260 C. Similar results were found in room temperature tests on 0.051 cm sheet tested in reversed bending (140). The notched fatigue behavior of 0.046 cm sheet of the Cb-752 and D43 was investigated at room temperature using tension-tension tests and a stress concentration factor of 4. The results indicated that for 10^7 cycles, the endurance limit would be 150 MPa for Cb-752 and 130 MPa for D43.

Summary

The mechanical properties of polycrystalline niobium and niobium base alloys have received considerable attention. The main features of the response to applied loads have been established. At low temperatures where the strength increases rapidly with decreasing temperature, brittle behavior is encountered and for pure niobium and most alloy compositions of interest the DBTT given by impact tests is below room temperature. At intermediate temperatures the strength changes slightly with temperature and is determined by the normal metallurgical variables such as grain size, deformation substructure, interstitial impurity levels, and composition. The available data suggest that a cell structure is formed at high levels of deformation in both niobium and its alloys and that the cell walls are weak boundaries to slip. In pure niobium the strength decreases at > 650 C due to the onset of recovery and recrystallization processes. A very considerable increase in strength may be achieved by alloying, both through the addition of solid solution strengtheners and/or finely divided second phase particles. The alloy additions also increase the recrystallization temperature and the strength is retained until higher temperatures. However, the strengthening is only effective up to 1400-1600 C and high strength at lower temperatures is only gained at the expense of ductility.

At high temperatures, creep processes become the major concern and these have been very widely studied in both pure niobium and niobium base alloys at temperatures $>0.5T_m$. The creep characteristics are very sensitive to test

vacuum and interstitial impurity levels. The creep behavior of pure niobium follows the classical pattern of primary, secondary and tertiary creep, the presence of each stage being determined by temperature and stress levels. Both solid solution strengtheners and second phase particles lead to greatly enhanced creep strengths $(>.5T_m)$, the elements tungsten and molybdenum and

second phase particles of zirconium carbide are particularly effective. The measured activation energy for steady-state creep in pure niobium in this temperature range is usually close to the self-diffusion energy although considerable variation is observed which may partly be due to substitutional strain ageing effects.

A recurrent theme throughout this review of the mechanical properties is the very important role played by interstitial impurities in determining the mechanical response of both niobium and niobium base alloys. Virtually every aspect of behavior is influenced by the presence of carbon, oxygen, nitrogen and hydrogen. This is better established in niobium than in the niobium base alloys and the data reviewed in the sections "Composition of Niobium and Niobium Base Alloys" through "Fatigue" are summarized in Table XXII. Perhaps the most important practical consideration is the loss of ductility which may result from high levels of these impurities, both at low and intermediate temperatures.

Table XXII, Influence of Interstitial impurities on metallurgical processes in pure niobium.

Metallurgical Property	Influence of Interstitial Impurities
Substructure formed under deformation	Some evidence that cell formation affected by interstitial impurities
Recovery	No strong evidence in the literature but some dependence likely
Recrystallization	Recrystallization temperature increased by presence of interstitials. No information on the effectof specific interstitial impurities
Mode of Fracture	Sensitive to location of interstitial impurities
Ductile-Brittle-Transition	DBTT increased significantly by oxygen and nitrogen. Nitrogen causes larger increase than oxygen (per wppm),
Slow strain-rate embrittlement	Ductile-brittle-ductile behavior observed at levels below the solubility limit. Oxygen embrittlement at 335-725 C. Hydrogen embrittle- ment at <0°C. No detailed work on nitrogen.
Short-time tensile tests	 Interstitial impurities give rise to: Yield point phenomena Dynamic strain ageing; oxygen 200-350 C Carbon 400 C, Nitrogen 450-600 C Solution hardening. Nitrogen more effective than oxygen at 20 C
Creep Properties	Oxygen and carbon give rise to creep strength- ening. Some disagreement in the literature on the exact effect of oxygen.
	No detailed information on nitrogen.
Fatigue	Very limited data - Oxygen strongly influences fatigue.behavior at 250-500 C.

The data reviewed illustrate that the changes in the mechanical properties of niobium by alloying have been very well established for the Group IVA, VA, VIA elements and it may be convenient to summarize the main effect of each element. The Group Va and VIA elements are considered in Table XXIII, Those elements which improve the short-time tensile properties do not necessarily give good high temperature creep strength; as exemplified by the behavior of vanadium. Of the elements considered, tungsten is the most potent creep strengthener while vanadium is the most effective element for producing alloys with good high temperature tensile properties. The Group IVA elements are best considered through their formation of second phase particles. Table XXIV lists the advantages and disadvantages of the carbides and nitrides formed by the reactive elements zirconium and hafnium. Carbides have been successfully employed in the development of high strength alloys

Table XXIII. Summary of effect of different solid solution strengtheners.

Ele- ment	Short-time Tensile Properties	High Temperature Creep Properties	Temperature	Low Temperature Ductility	Other Comments
W	Not as good as Mo or V	Most potent creep strengthener	All Increased	Lowered-Degrades fabricability	Density and melting point Increased
Мо	Most effective at temp- eratures <1100 C.	Limited strength- ening	All Increased	Lowered	Density Increased
v	Most effective of all Group VA and VI Elements for improving high temp. tensile properties	Rapid diffuser in Nb -Not particularly effective for high temperature creep properties	Little effect in comparison to Mo or V	Little effect in comparison to Mo <i>or</i> W	Most useful for low density alloys for medium temperature applications
Та	Little effect	Some strengthening at > 10 atomic percent	Little effect	-	Considered to be non- strengthening although it increases alloy melting point and density
Cr	Limited solubility but at concentrations below solubility limit quite an effective strengthener	-	-	-	Tendency towards embrittlement-limited to < 3 percent Improves Oxidation resistance

Table XXIV. Summary of effect of different Second - phase strengtheners.

Reactive Metal (Zr, Hf)	Advantages	<u>Disadvantages</u>	Other Comments
CARBIDES'	Produce high short-term and long-term strengthening Generally good thermal stability up to 1200-1300 C Thermo-mechanical treatments may be used to optimise carbide structure.	Lead to low room temperature ductility. At >1300 C carbide coalesence and loss of strength occurs	Most widely studied of the three articles optimum levels. 0.1-0.35 wt. % for Nb-Zr-C with atomic ratios of Zr/C between a and 2. 0.1-0.15 wt. % for alloys also containing W, Mo or V. Levels above this lead to coarse grain boundary precipitates and loss of ductility.
NITRIDES'	High thermodynamic stability – Nitrides stable up to 1600– 1700 C. Thermo-mechanical treatments give little control of nitride distribution.	High volume fractions required to achieve high strength. Cannot be achieved without exceeding solubility limit at Melting Point. (Nitride formed on solidifica- tion are fairly uniformly dis- tributed and with sizes that lead to strengthening).	Most extensively studied in Nb- Zr-N. Although some studies of HFN Optimum strengths with 3.5 vol. % of nitride and Zr/N (~1.6-1.7 atomic ratio). - 3 mol. % of HF gave good strength properties.
OXIDES	Zirconium containing alloys may be strengthened by internal oxidation. Finely divided precipitates at <.05µ	Difficult to control particle size at high oxygen concentrations. At levels required for appreciable strengthening coarse oxides formed which reduce ductility.	Not as successful as nitrides or carbides, largely through difficulty of controlling particle. size.

1 See ref. (100) for a review of the dispersion hardening by carbides and nitrides.

responsive to thermo-mechanical behavior. Alloys with the optimum volume fraction of nitrides have been developed in the USSR (but the higher thermodynamic stability of the nitrides is offset by the difficulty of obtaining a suitable distribution). Finally, appreciable strengthening has <u>not</u> been achieved by distributions of oxide particles because of the difficulty of obtaining suitable distributions.

Irradiation Behavior of Niobium and Niobium Base Alloys

Introduction

A wide diversity of irradiation produced phenomena have been studied ranging from fundamental aspects of behavior to the investigation of problems associated with the application of niobium as a structural material for inreactor core components. It is difficult in reviewing such a range of topics to identify a unifying theme but the aim will be to describe typical behavior and demonstrate that in many processes the interstitial impurities again play an important role. The organization and content of this part of the review is as follows. Firstly, the interaction of fast neutrons with niobium will be described since this is central to the use of niobium in a reactor environment, The second section is concerned with properties of the irradiation produced point defects. This is followed by a discussion of the surface erosion caused by ion and neutron bombardment which has received considerable interest in the literature since the emergence of niobium in the early 1970's as a candidate material for the first wall of a fusion reactor. Finally, the development will be reviewed of the irradiation produced microstructure created by fast particle irradiation and the effect this has on the mechanical properties. It will become apparent that most of the attention in this general area has been focused on pure niobium with relatively little interest in niobium-base alloys other than niobium zirconium alloys.

Neutron interactions with niobium

<u>Introduction</u>. When a metal is irradiated with a flux of fast neutrons, the neutrons lose energy through interacting with the atoms of the solid. The principal sources of radiation damage to the solid are the displacement of atoms from their lattice sites and the introduction of foreign atoms through transmutation reactions. The other important considerations to the application of materials in a reactor core are the absorption of the incident neutrons and the radioactivity induced in the solid from continuous exposure to the neutron flux. All these processes are strongly dependent on the neutron energy spectrum and the atomic composition of the solid. These neutron interactions with niobium are discussed below.

A precursor to this discussion is to detail the principal sources of neutrons of interest at the present time. Fission reactors fall into two categories, thermal and fast. In both reactor designs, the neutrons are created in the splitting of a fissile atom, such as uranium-235. In thermal reactors, the neutrons are moderated by a suitable material such as graphite or heavy water and their energies extend from several WeV down to thermal energies. In fast reactors, there is no moderator and as a result, the neutron energy spectrum is peaked at higher energies than in a thermal reactor. In the proposed fusion reactors, the neutrons are generated by the fusion of the isotopes of hydrogen with an energy 14.1 MeV. This is a considerably higher energy than the neutron energies typical of fission reactors. The great interest in fusion neutron interactions and the lack of suitable neutron sources had lead to the development of accelerator based devices, e.g. RTNSII, where low fluxes of these high energy neutrons are produced. The characterisitics of the neutron energy spectrum in representative fission and fusion sources are given in Table XXV and are discussed below.

Fast neutron-lattice atom collisions. Frequently in fast neutron lattice atom collisions, the energy imparted to the recoiling lattice atom is sufficient to displace it from its lattice site, creating a Frenkel defect, i.e. a vacancy (empty lattice site) and an interstitial (an atom occupying a nonlattice site). Thus a most important consideration when a metal is irradiated with a flux of fast neutrons is the evaluation of the number of displaced atoms. This is dependent on the number of lattice atom-fast neutron collisions, the energy spectra of the recoiling lattice atoms, and the energy required to displace a lattice atom. This displacement energy is dependent on the direction the recoiling atom moves in relation to the crystal axes; in niobium, Lucusson (144) gives the minimum energy required to displace an atom as 36 eV and the average energy as 78 eV. The cross-section for neutron collisions and the energy spectra of the recoiling atoms can be evaluated using the damage models which compute the primary recoil spectrum for any desired neutron energy spectrum from the energy dependent neutron crosssections. In Tables XXVI to XXVIII presents the characteristics of the energy spectra of recoiling atoms and the displacement damage produced in niobium by different sources of fission and fusion neutrons calculated using the code RECOIL (145). The neutrons in the fission neutron spectra are of a considerably lower energy than those from fusion devices, particularly with respect to the fraction of neutrons with energies above love (see Table XXV). The total cross-sections for producing a recoil do not vary appreciably from neutron source to source and are always in the range 4-7.5 barns (Table XXVI). However, the recoil energy distribution is very dependent on the neutron energy spectrum (Table XXVI). The recoils created by fission neutrons arise primarily from elastic reactions where the kinetic energy is conserved, and are peaked at energies below lkey. In contrast, the majority of the recoils created by fusion neutrons arise from inelastic and nonelastic recoils particularly in 2n where the struck atom is left in an excited state and decays emitting a particle or gamma ray. These recoils are frequently above 60-100keV and this results in a recoil spectrum with far more high energy recoils than created by fission neutrons. The highest energy recoils created in each source are particularly effective at creating displacement damage (Table XXVII), For example, only 2.4 percent of the recoils in a fast reactor are above 30keV but they are responsible for 20 percent of the damage. The neutrons produced by fusion reactors are considerably more damaging than the neutrons produced in fission reactions (Table XXVIII). At the fluxes typical of each source (Table XXVIII), it can be seen that the times taken whereby each atom in the lattice has been displaced once (i.e. 1 dpa) are guite short particularly in the case of the fast reactor and CCTRII. The microstructures developed under such high doses will be reviewed in the section "High-dose Irradiations".

<u>Transmutation products</u>. A second important aspect of neutron irradiation is the transmutation products created in the.non-elastic collisions. The most important transmutation products are the gaseous impurities, hydrogen and helium, which affect the properties of the metal even at low concentrations. In Table XXIX, the gas generation for niobium in typical fast and

	Table >	αv.	Char	acteristic	s of the	Energy	Spectra o	of		
	Different Neutron Spectra									
			(1)	(2)		(3)		(4)		
		CCTR	11	RTNS II	Fast Re	actor	Thermal H	Reactor		
>10	Mev	23.8	%	100.0%	0.0	18	0.0	1%		
>1.0	Mev	43.5	%	100.0%	11.9	%	6.7	%		
>0.1	Mev	73.7	%	100.0%	57.3	%	17.9) %		
Average	Neutror	ı								
Energy	(Mev)	4.1	1%	14.0%	0.45	5%	0.2	3%		

(1) First Wall of Culham Conceptual Tokamak Reactor (Fusion neutrons)

- (2) Rotating target neutron source; D-T neutrons (~14MeV) (Fusion neutrons).
- (3) FD5 fast reactor spectrum 'Fission neutrons)
- (4) In hollow fuel element in PLUTO materials testing reactor (Fission neutrons).

Table XXVI. Characteristics of recoil spectra for Nb irradiated in different fast neutron sources

	Percentage of recoils E							
Recoil Energy, E (keV)	CCTR II ⁽¹⁾	RTNS II ⁽²⁾	(3) Fast Reactor	(4) Thermal Reactor				
01	92.0	99.6	90.3	48.7				
1.0	70.3	96.4	62.2	33.0				
5.0	42.0	84.8	26.9	8.1				
10.0	28.3	73.4	12.5	4.8				
30.0	13.0	52.5	2.4	1.6				
60.0	9.4	47.8	0.8	0.5				
100.0	7.0	42.6	0,1	0.1				
200.0	2.4	18.7						
500.0	0.14	1.1						
ross-section for	6.41	3.98	7.67	6.88				

Total cross-section for creating a recoil (barns)

Recoil

Table XXVII. Percentage of displacement damage produced by recoils with energy > 5*.

Percentage of displacements created by recoils with energy > E

Fnermy F		-		
(keV)	CCTR II	RTNS II	Fast Reactor	Thermal Reactor
0,1	99.9	100	99.9	99.8
1. 0	99.2	100	96.3	94.3
5.0	94.6	99.4	74.1	72.1
10.0	88.9	98.2	53.0	60.8
30.0	75.1	93.5	22.2	35.7
60.0	67.1	91.5	8.9	16.2
100.0	54.5	87.2	2.3	4.5
200.0	25.0	38.4		0.4
500.0	0.8			

Calculated assuming displacement energy = 40eV.

Table XXVIII.	Density of	damage	produced	i n	the	four	different	sources.

Source	CCTR II	RTNS II	Reactor	Reactor
Displacements per atom for a flux of one neutron $\mathbf{m}^2 \times 10^{26}$	9.4	25.3	2.9	1.2
Time required at typical flux levels to produce 1 dpa (sec)	5(a) 8.9 x 10 (10.3 days)	(b) 9.9 x 10 ⁶ (114.5 days)	2.3 x 10 ⁵ (2.7 days)	7 (d) 1.1 x 10 (127.3 days)
(a) $1.2 \times 10^{19} \text{n/m}^2/\text{s}$	sec (c)	1.5 x 1022 n/	m²/sec	
(b) $4 \times 10^{17} n/m^2/s$	sec (d)	7.5 x 10 ¹⁸ n/m	f/sec	

Table	XXIX	. 1	Rates	of 1	proc	luctic	on of	disp	lace	ements	and
He	lium	and	Hydro	ogen	i n	fast	and	fusic	on re	eactors	

	Displacement	Gas Prod	luction rate	Gas Produc	tion rate	Displacement
	damage dpa/s	appm/s	<u>. (x 10/)</u>	appm/s.	(x 10 ^{-/})	damage dpa/s
	10 ⁻⁷	He	H	He	H	$(x \ 10^{-7})$
A1	23.8	7.4	24.0	112	104	4.63
Fe	9.93	2.8	35.3	51.1	153	51.1
Сr	11.4	1.3	11.7	79.7	135	79.7
Ni	11.0	29.7	424.0	69	801	69.0
Mn	11.8	1.4	10.5	34.9	250	34.9
Nb	7.51	0.69	4.1	9.83	85.5	9.83
V	12.4	0.40	7.3	17.0	144	17.0
Тi	14.9	1.7	2.7	49.3	100	49.3

(a) Neutron wall loading = 1MW/m²
(b) Data from Gabriel, Biship and Wiffen, Nucl. Technol. 1978, <u>38</u>, 427.
(c) Data from Jarvis (143).

fusion reactors is compared to the major constituents of other structural materials; both the helium and hydrogen production are lower in niobium than the other materials. The helium production is higher in the fusion reactor because the (n,α) cross-section is high for the 14MeV neutrons which are a major component of the fusion neutron spectrum (see Table XXV).

The primary solid transmutation product of niobium is zirconium, Jarvis (143) calculated that in the first wall of a fusion reactor with a wall loading of $1.25MW-yr/m^2$ the zirconium content of Nb-lZr would increase to 5.3 percent after 37.5MW-yr/m².

<u>Neutron absorption</u>. An important consideration for the use of any metal in a reactor core is its absorption of neutrons. In the fast reactor, for example, the absorption of 100keV neutrons must be low as these neutrons are important for the breeding of plutonium; an absorption cross-section of about 10 mb is considered acceptable. Table XXX contains the cross-sections for various alloy elements (146) and it can be seen that although Nb has a lower cross-section than tungsten or tantalum, it is far higher than the elements contained in austenitic steels (Fe, Ni and Cr). This unacceptably high cross-section is one factor which precludes niobium from use in the core structure of commercial fast reactors.

Thermal neutron cross-sections are also presented in Table XXX and it is clear that niobium has a low cross-section in comparison with the other elements listed. Indeed only aluminium, berylium, magnesium, and zirconium have lower values for this parameter. The low value for zirconium has lead to the development of zirconium base alloys for use in thermal reactors.

Induced Radioactivity. The rate at which the radioactivity induced in a structural material decays has become an important parameter in the selection of candidate materials for the first wall of fusion reactors. In Figure 25 the decay of the induced radioactivity is compared for different alloys irradiated for two years at 1.25MW/m² in CCTRII (143). The decay times for Nb-12r are comparable with the other materials over the short term (≤ 10 years), but the activity of ⁹⁴Nb gives an unacceptably high level of activity over the long term. This is a major barrier to the use of niobium as a containment material in a fusion reactor since it precludes easy handling after shutdown and raises problems for the eventual reprocessing of activated material.

Metal or alloy element	σ (100 keV) nγ (mb)	Thermal neutron cross-section (barns)
A1	4	0.232 ± 0.003
Fe	6.1	2.56 ± 0.05
C r	6.8	3.1 ± 0.2
Ni	12.6	4.51 ± 0.1
Zr	15.1	0.182 ± 0.005
Mh	25.6	13.3 ± 0.1
Mo	71.0	2.65 ± 0.05
Nb	100.0	1.15 ± 0.05
W	178.0	18.5 ± 0.5
Та	325.0	22 ± 1
Hf	-	103 ± 3

Table XXX. Absorption Cross-Sections for Metals and Alloy Elements (146).



Figure 25. Decay of induced radioactivity for the CCTR II breeding blanket (143).

Properties of Point Defects Generated by Irradiation

Point defect formation and migration energies are particularly important in determining the irradiation response of any metal. In niobium these energies are not experimentally well established but there is information on the temperatures at which the point defects are able to undergo long-range migration. This has been obtained primarily from electrical resistivity measurements of the recovery of specimens irradiated at low temperatures and subjected to isochronal anneals.

In niobium and other Group VA metals, the recovery stages have been found to be extremely sensitive to impurity content (147). However, in ultrapure material Fuss and Schultz (148) have recently presented evidence that interstitial point defects created by 3.5MeV electrons at 4.5K are already mobile at 4.5 K, and the authors note that all the Group VA metals show indications for long-range migration of point defects at or below 4 K. The temperature at which vacancy point defects undergo long-range migration appears to be uncertain, although Faber and Schultz (149) in ultra-high purity niobium found a recovery stage at 250 K, which was suppressed by the presence of interstitial impurities and had the expected properties of an intrinsic Stage III (2nd order kinetics). In many fcc and bcc metals, this stage is thought to be due to single vacancy migration and the annihilation of interstitial clusters. However, Seeger and co-workers (149) have proposed an alternative model for Stage III based on two configurations for the interstitials one of which is mobile in Stage III and one at lower temperatures.

The sensitivity of the annealing stages in irradiated niobium to the presence of small concentrations of interstitial impurities suggest that there are strong interactions between these impurities and point defects. Table XXXI taken from Kaim summarizes information on the break-up of impurity point defect complexes and the free migration of the impurity (147). The

References	<u>(</u> 1	Impurity dependent stages preak-up of complexes)	Stages due to free migration of the impurity
(150) (151) (152) Faber <u>e</u> t al 3MeV e irradiation at 4 K		58K O and N 390K O and N (0,N doped samples)	450K - 0 540K - N
Donitz et al (153) Vavra et al (154) Neutron - irradiation at 4.6 - 7 K		62K O and N 135K - Especially N	>250K - 0 and N
Pichon et al (155) Electron-irradiation at 20.4 K		215K - O	
Diehl (156) Neutron-irradiation		60-70K - N	
Brown et al (157) Neutron-irradiation at	18 K		445K O

Table XXXI, Break-up of impurity point defect complexes.

stages found at or below 150K are thought to be due to the break-up of impurity-interstitial point defect complexes, while those giving rise to stages above- 250 K are due to the break-up of complexes formed by impurity and the Stage III defect.

Point defect mobilities are one of the parameters which control the defect microstructures developed under irradiation. It is clear from the results given above that irradiation by displacement producing fast particles at temperatures >4 K will produce self-interstitial atoms which are mobile and able to interact with pre-existing dislocations or cluster to form interstitial loops and/or interstitial point defect impurity complexes. Although the temperature at which vacancies undergo long range migration is uncertain, it is likely that they will be mobile at the elevated temperatures of interest in reactor applications, and thus a complex microstructure will be created by the point defects generated in the irradiation. This is discussed in detail in the section "Development of the Irradiation Induced Microstructures".

Surface Effects

Attention in this area has concentrated on the erosion of the surface by energetic fast particles. The major mechanisms whereby this occurs are by the physical sputtering of surface atoms due to the impact of energetic particles or by blistering which occurs when high concentrations of gas atoms implanted below the surface cause the surface skin to blister and erode. The requirements for data on the probable plasma: surface interactions in fusion devices has led to considerable interest in the surface erosion of pure niobium. (For a review of surface effects in controlled thermonuclear fusion, see reference 215).

<u>Sputtering</u>. The number of sputtered atoms is proportional to the number, energy, **mass** and angle of incidence of the incoming particles. In a discussion of a physical sputtering model for fusion reactor first-wall materials, Smith (158) presented the data available (1978) for heavy and light ion sputtering of niobium; these data are given in Figure 26. The observed sputtering yield increases with energy for heavy-ions (Ar and Nb⁺) with values between 10⁻² and 10. The sputtering yields for light-ions are lower than for heavy-ions and show a more complex energy dependence with a maximum at ~2.5keV. The calculated curves are taken from the semi-empirical physical sputtering theory developed by Smith, where the general shapes of the curves are based on theoretical considerations but the magnitudes of the yields are determined primarily from experimental data. They give a reasonable agreement with the experimental data.

The physical sputtering of niobium by energetic fusion neutrons (14.1 MeV) has also been reported. The reported yields (159) are considerably lower than the sputtering yields for ions. Typical values are in the region 10^{-5} to 10^{-4} atoms sputtered per incident 14MeV neutron which is in agreement with theoretical predictions. In addition to sputtered atoms, Kaminsky and coworkers (160-163) reported that depending on sample preparation, chunks of niobium were emitted after 14MeV neutron irradiation; typical chunk dimensions were $0.1-5\mu$ m and they formed the major part of the material removed from the surface dimensions. The number of chunks emitted is reported to be greater in cold-rolled Nb than in annealed Nb while no chunk emission was found in single crystal niobium. Some controversy still exists regarding both the mechanism and conditions under which chunks are observed. For a detailed discussion of chunk emission and neutron sputtering, see Behrisch (159).



Figure 26. Plot of experimental sputtering data and comparison with calculated energy-dependent physical sputter-yield curves (158).

<u>Blistering.</u> The processes leading up to blister formation are envisaged to be as follows. When a metal is implanted with energetic gas ions, the ions will lose energy in the creation of lattice defects and come to rest in a narrow region near the end of this range. If the implanted gas atoms have a low permeability in the solid they will combine with vacancies and form bubbles; as the dose increases, the bubble density will increase, and bubbles will interconnect and grow to large diameters. Eventually, the stresses set up by this population of bubbles will cause blisters to form on the surface, and the peeling of the blister skin will cause erosion.

Blistering in pure niobium created by implanting the isotopes of hydrogen and helium has been studied extensively (164-180). The dependence of the size, shape and density of the blisters on the principle experimental parameters has been established and representative results are presented in Table XXXII for monoenergetic irradiations. A comprehensive blistering theory does not exist at present and thus a qualitative discussion of these results has only been presented in the literature.

Studies of blistering of niobium have been particularly useful in elucidating the mechanisms underlying this phenomenum. Kaminsky and co-workers (175) have demonstrated from examining blisters created in niobium by H⁺ ions with energies in the range 500-1500keV, that the average skin blister skin thicknesses correlate more closely with the range of the He⁺ ions rather than the maxima in the damage energy distributions. These results are in agreement with the model for blistering based on the internal gas pressure being the driving force for blister formation. An alternative model has been discussed in the literature based on the concept that blistering arises from the relief of the lateral stress set up by the distribution of bubbles in the near surface regions (182). For reviews of blistering models see Roth (182) and Das (183).

A further important aspect of blistering in niobium is that it is known (181) that helium blistering in the low energy range ($\langle 20 \text{ keV} \rangle$) is replaced by micro relief after one generation of blisters due to significant surface erosion by sputtering. However, evidence at high energies is in conflict, Behrisch et al (173) report a sponge like surface structure after a high dose

Parameter	Dose, C/cm ²	Energy (keV)	Low	Temp. <u>°C</u>	Specimen	Blister Data
Comparison of He and D (169),(174),(184	1.0 4)	500	D He	20 C 20 C	Polycrystaline Polycrystaline	No Blister 3-30µ diameter 2 x 10° blisters/cm
Ion Energy (165)	0.1 0.5 0.5 1.0	4 100 250 500	+ He+ He+ He+ He	R.T R.T. R.T. R.T.	Polycrystaline Polycrystaline Polycrystaline Polycrystaline	0.4 μ diameter 1-3% 2 x 10 ⁶ /cm ² 3-30 μ 1.2 x 10 ⁶ /cm ² 1 large blister
		1500	He ⁺	R.T.	Polycrystaline	occupying 2/3 of irradiated area 1 large blister
Tradiation Temperature (164)	0.1 0.01		He H e+	п.т. 900 с	Polycrystaline Polycrystaline	No Blisters Blisters

Table XXXII. Representative Blistering Data for Nb.

Irradiation Conditions

of $20C/cm^2$ 100keV ⁴_{He} ions while Kaminsky et al (184) reported repetitive blistering in polycrystalline niobium irradiated at 400 C with the same energy ⁴_{He}⁺ ions.

Recently, Terreautt (180) has considered the available experimental evidence for repetitive blistering and demonstrated that the observed behavior correlates with the relative width of the implantation profile, W $_{\rm R}$. Three distinct regimes were found:

W _R > 1	single generation of blisters
0.7 < W _R < 1	slow disappearance of blistering
$W_{\rm R}^{\rm <} -0.7$	repetitive blistering or flaking

For niobium, repetitive blistering is predicted to occur at above ~50keV.

The data on blistering in Nb base alloys is of a very limited nature. Englin (185) has studied blistering in Nb-12; and found that after implanta-

tion with He⁺ ions blistering was only observed after annealing at 950 C for two hours. The blister size increased with increasing ion implantation energy annealing time and temperature. As in pure metals multi-energy implants produced smaller blisters compared to single ion energy implants.

Development of the Irradiation Induced Microstructure

During fast-particle irradiation at temperatures where either or both vacancy and interstitial point defects are mobile, a complex microstructure will develop as the point defects which do not recombine cluster of diffuse to the different point defect sinks. Depending on the precise irradiation conditions the microstructure might consist of dislocation lines, dislocation loops (vacancy or interstitial), gas filled bubbles, voids and precipitates. The microstructures developed at low doses of fast particles have been studied in pure niobium and will be reviewed in the section "Low-dose Irradiations". The more complex microstructures evolved at doses where every atom has experienced multiple displacements has been studied primarily in niobium and niobium-zirconium alloys and will be reviewed in the section "High-dose Irradiations". It is to be noted that the majority of results obtained in these studies have come from transmission electron microscope studies.

Low-Dose Irradiations

Fast neutron irradiations. The defect structure of niobium after fast neutron irradiation was first described by Tucker and Ohr (186). Since then there have been numerous studies of the damage created by fission neutrons and more recently fusion neutrons. The majority of authors report a uniform distribution of small defect clusters and dislocation loops, the density and size of which are dependent on the precise irradiation conditions and most importantly the purity of the material. Representative results are given in Table XXXIII for both fusion and fission neutrons. Both vacancy and interstitial loops have been reported, the vacancy loops are formed from the collapse of the vacancy rich centers of collision cascades and the interstitial loops by nucleation and growth of clusters formed by the rapidly migrating interstitial point defects. The data of Agyrawal et al (189) demonstrates the important effect oxygen has on the density and diameter of the defect clusters and points to the important role played by interstitial impurities in the nucleation of point defect clusters in niobium. It is interesting to note that the total area of dislocation loop decreases with increasing oxygen content as this suggests that the impurity is increasing the level of point defect recombination.

Table	XXXIII	A.	Results	of	Fission	Neutron	Irradiation.
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Ref	Dosq n/m	<u>Temp C</u>	Defect Cluster Density /m	Vacancy Interstitial n	Size Range ature (nm)
	(E>0.lMeV	7)			
186	2 x 10 ²² (a) 50	5 x 10 ²¹	No information	2.0-10.0
187	2×10^{21}	80	0.6 x 10 ²¹		1.5-6.0
	6 x 10 ²¹		1.4 x 10 ²¹		1.5-10.1
	8 x 10 ²¹		3 x 10 ²¹	~2/3 Interstitial	1/3 vacancy 1.5-20.1
	1.6 x 10 ²²		4.8 x 10^{21}		-
	6 x 10 ²¹	4.2 K	0.7 x 10 ²¹	~1/2 Interstitial	1/2 vacancy -
188	1.8 x 10^{21}	30	-	~2/3 Interstitial	1/3 vacancy 1.5-3.0
189	9 x 10 ²³	80	7×10^{21}	(1) -	$\bar{d}^* = 16.5$
(stu	died)		54 x 10 ²¹	(2) _	6.0
(eff	fect of		90 x 1021	(3) –	3.0
oxyg	gen)		127×10^{21}	(4) -	2.5
	(1) 10 pp (2) 250 pp	o≖ oxygen m oxygen	*	ā = mean size (nm) a) E > 1MeV	

(3) 480 ppm oxygen

(4) 904 ppm oxygen

Table XXXIII B. Results of Fusion Neutron Irradiation.

<u>Ref</u>	Dose_n/m ²	Cluster 3 <u>Density</u> /m	Vacancy <u>Interstitial nature</u>	Size Range (nm)
188	5 x 1021	_	2/3 Interstitial 1/3 vacancy	1.5-3.0
190	1–2 x 10 21	-1×10^{22}	-	d [*] – 4

The loop distribution produced after fusion neutron irradiations are generally found to be similar to that produced by fission neutrons (188, 190). Roberto et al (208) report that the damage retained in cluster form per neutron is - 2.5 times higher for aa-Be neutron with a mean energy of 15MeV compared to a fission reactor neutron. This value compares favorably with the ratio derived from the calculated damage production for each neutron source.

In contrast to the uniform distribution of small defect clusters discussed

above Chen et al (191) reported that after an irradiation to 8×10^{23} fusion n/m^2 (E > 0.1MeV) a population of large defect clusters coexisted with a population of small defect clusters. These large defect clusters were not simple dislocation loops but were raft-like structures containing many subclusters. At lower doses in niobium containing 10 and 68 ppm oxygen Loomis and Gerber (192) also observed large defect clusters composed of numerous small subclusters.

<u>Charged particle irradiation</u>. Kaim and Palmer (193-4) have studied 2MeV ⁴He⁺ irradiation of neutron doped with oxygen using Rutherford backscattering techniques. In particular they obtained interesting data on irradiation induced lattice-site change of oxygen after 2MeV ⁴He⁺ irradiation at 86K and 293K. In unirradiated niobium oxygen occupies octrahedral sites but after irradiation the lattice site is altered and the results were consistent with oxygen atoms displaced by 0.05 \pm 0.01nm with the displacements occurring with equal probability in the different <100> directions. They also demonstrated that the effect of oxygen is to enhance the retention of interstitials in clusters.

<u>High-dose irradiations</u>. It is well established that the dislocation lines and loops produced during irradiation are biased sinks for interstitial point defects and that this creates an excess of vacancies in the lattice. These vacancies are only able to form a neutral sink **as** any biased sink, such as a vacancy dislocation loop, will be inherently unstable through the excess of interstitials flowing into it. The most frequently observed neutral sink are three-dimensional voids which require some form of nucleating agent, such as gas atoms, to stabilize the void embryo against collapse. Void formation is generally limited to temperatures where vacancies are mobile $(\ge .3T_m)$; they also do not grow at very high temperatures $(>0.5T_m)$ because the vacancy supersaturation **is** not usually high enough to keep the voids from evaporating.

The production of voids in metals, particularly in those alloys considered for use in fast reactor core components has been very extensively studied. Although void swelling in neutron and ion irradiated niobium has been fairly widely studied, Nb-12 τ is the only niobium base alloy that has received any attention in the literature. As in other metals, most emphasis has been placed on determining the void swelling characteristics at elevated temperatures. However, the development of all elements of the microstructure are clearly interlinked and wherever possible both void and dislocation data will be given.

Fission neutron irradiation

<u>Pure Niobium</u>. The general features of void swelling of niobum have been studied as early as 1971 and the results are summarized in Table XXXIV. The early data of Wiffen (195) and Michel and Moteff (196) indicated that the temperature for maximum swelling was approximately $600 \text{ C} (\sim 0.32T_m)$ but more

recent data from Jang and Moteff (197) suggests that the maximum swelling is -1050 C. In all cases the void density decreases and void size increases with increasing irradiation temperature. The higher swelling and the very marked temperature dependence of the void numbers and sizes found by Bartlett et al (198) were not observed by Michel and Moteff (196) and these differences may arise through compositional differences between the casts of "commercial purity" niobium. This and the slightly higher dose employed by Bartlett et

al (198) may also account for the differences in the dislocation component of the microstructure observed in the two studies. In both cases the dislocation line density decreased with increasing temperature, but Bartlett et al (198) only observed dislocation tangles while Michel and Moteff (196) observed a population of dislocation loops. Their data are compared in Table XXXV.

		Voi	Void Parameters						
Tempera- ture C	Fluence Neutrons/m ² >1MeV	Concentration tion yoids/	Av∎ Diam. (nm)	Volume Fraction %	Ref				
425	3.7 x 10 ²⁶	1.6 x 10 ²³	7.0	3.1	195				
585	3.7 x 10 ²⁶	2.1 x 10 ²³	7.1	4.8					
790	3.7 x 10 ²⁶	2.8 x 10 ²³	18.6	1.04					
425	2.5 x 10 ²⁶	23 x 10 ²²	5.5	0.23	196				
585		2.9 x 10 ²²	6.1	0.37					
790		8.7 x 10 ²⁰	15.6	0.21					
470	3.9 x 10 ²⁴	3 x 10 ²²	2.0	0.01	200				
650	5.5 x 10 ²⁴	8 x 10 ²¹	6.0	0.09					
750	4.1 x 10 ²⁴	5×10^{20}	12.5	0.05					
600	5×10^{24}	1 x 10 ²²	5-6	0.1–0.2	199				
900	5 x 10 ²⁴	0	0	0					
430	1 x 10 ²⁶	-	-	0.18					
580	1 x 10 ²⁶	-	-	0.2					
700	1 x 10 ²⁶	-	-	0.2	197				
800	1 x 10 ²⁶	-	-	0.4					
900	1 x 10 ²⁶	-	-	0.4					
1050	1 x 10 ²⁶	-	-	0.5					
450	3.4 x 10 ²⁶	8.5 x 10 ²³	4	2.9					
550	3.9 x 10 ²⁶	1.9 x 10 ²²	14.1	2.9	198				
600	3.9 x 10 ²⁶	3.1 x 10 ²¹	25.3	2.7					
625	5.4 x 10 ²⁶	2.1 x 10 ²³	4.6	1.5	230				

Table XXXIV. Void and Swelling Data for neutron-irradiated niobium.

<u>Nb-Zr alloys</u>. At these high doses the addition of zirconium radically alters the development of the microstructure. In alloys containing 1 percent Zr the data, (196, 197) suggest that appreciable void swelling only occurs in a relatively narrow temperature region about 800 C (Table XXVI). The data on alloys with higher zirconium contents (198) indicate that this void resistance is maintained at least at temperatures below 800 C (Table XXVI). The zirconium additions also modified the dislocation structures observed (Table XXXVII). In Nb-1Zr the size and density of the dislocation loops present in the microstructure were increased in comparison to pure niobium irradiated under the same conditions (196). While at higher zirconium contents the dislocation loops and tangles were no longer homogeneously distributed (198).

Several reasons have been put forward to explain the suppression of void swelling by zirconium additions. Michel and Moteff (196) concluded that the suppression of void formation at 425 C and 585 C was due to vacancy trapping at the oversize solute atoms and that the simultaneous migration of oxygen and/or nitrogen or carbon and vacancies was responsible for the nucleation of voids at 790 C. Bartlett et al (198) also considered that the high dislocation density in the alloys and the effective fall in the concentration of the surface active gases oxygen and nitrogen might also be factors in suppressing void formation.

<u>Nb-Mo alloys</u>. Michel and Smith (229) have reported results of neutron irradiation of niobium and five niobium-base alloys to -4 dpa at 482 C (229). Voids were observed in niobium and Nb-1Mo. None were found in Nb-1Zr, Nb-5Mo, Nb-1OMo or Nb-5Mo-1Zr alloys; this the authors suggested that vacancy trapping at oversize solutes was responsible for the suppression of swelling in these alloys.

<u>Ion irradiation</u>. The high atom displacement rates created during heavyion bombardment makes possible the attainment of high irradiation damage levels in a far shorter time than the equivalent fission neutron irradiation. In contrast to fast neutron irradiation where the neutron penetrates consider-

able distances the range of heavy-ions is very short $(\sim l_{\mu} \text{ for } 3\text{MeV} \overset{58}{}\text{N1}^+)$ and the damage layer may be only $\sim 0.l_{\mu}$ thick. The proximity of the damage layer to the specimen surface means that in niobium, the development of the damage microstructure produced by elevated temperature irradiation may be influenced by pick-up of oxygen and nitrogen during the irradiation from the accelerator vacuum. Indeed Loomis et al (201) consider that to avoid contamination effects irradiations must be carried out in a vacuum of $\sim 10^{-8}$ torr or better.

The void swelling in ion-irradiated niobium and Nb-lZr have been extensively investigated, particularly by Loomis and co-workers at Argonne National Laboratory who employed 3.5MeV Ni ions which have a penetration of 0.7μ . A far wider range of irradiation and metallurgical parameters have been examined than was possible under neutron irradiation and the main conclusions will be given below.

Pure Niobium. The dependence of the void parameters on irradiation dose has been established by Brimhall and Kissinger (202) at 800 C and 900 C. At doses below 10 dpa, the void swelling was approximately proportional with dose but at doses above this the void swelling saturated. These trends are illustrated in Figure 27 for an irradiation dose of 800 C. In agreement with this Loomis and Gerber (201) observed that the void parameters at 780 C and 957 C at a dose of 130-140 dpa were not significantly different to the parameters found at 50 dpa.



Figure 27. Plots of and void with 7.5 the dose dependece of void swelling number+density in niobium irradiated MeV Ta ions at 800 C (202).

			Void 1	Parameters		
<u>A1loy</u>	Tempera- ture (C)	Fluence n/m ² (E 1MeV)	Concentration	Average Diam. (nm)	Volume Fraction	<u>Ref</u> ,
Nb−lZr	425	2.5 x 10 ²⁶	-	-	-	
	585		-	-	-	196
	790		1.8 x 10 ²⁰	57.5	2.2	
	430	1×10^{26})		0	197
	580	1 x 10 ²⁶			0	
Nb-lZr	700	1×10^{26}) Not reported		0	
	800	1 x 10 ²⁶			2.3	
	900	1 x 10 ²⁶)		0.13	
	1050	1×10^{26})		0	
Nb-5Zr	600	3.9 x 10 ²⁶	2 x 10 ²⁰	12.5	0.02	198

Table XXXVI. Void and Swelling data for neutron irradiated Nb-Zr alloys.

Table XXXVII, Loop and dislocation data for neutron irradiated Nb-Zr alloys.

A110y	Irradiation Temperature		Plu _n/i	ence 2	Av.	Lo diam, (nm)	oops j	Der	sity /m ³	Dis: de	location ensity /œ ²	Ref.
Nb-12r	425	2.5	x	10 26	1	L0.0	7.3	x	10 ²²	4.2	x 10 ¹³	196
	585	2.5	x	10 26	1	11.0	7.3	x	10 ²²	3.4	x 10 ¹³	196
	790	2.5	x	10 ²⁶	3	33.0	7.1	x	10 ²¹	3.4	\times 10 ¹²	
Nb-5Zr	600	3.9	x	10 26	-	18.0	4.6	x	10 ²¹	1.1	\times 10 ¹⁴	198

In constrast to the neutron results, a complex temperature dependence has been observed (202) in both the void and dislocation loop parameters for niobium irradiated to 35-70 dpa by 3.0MeV Ni⁺ ions in the temperature range 600-1150 C. The most notable feature of the results was the double peak in both the void swelling and dislocation loop density illustated in Figures 28 and 29. In assessing the observed behavior, the authors noted that the oxygen and nitrogen pick-up in niobium increased dramatically with temperature and they suggested that the microstructure developed at high temperatures might be influenced by this. This interpretation was supported by the observation of niobium oxide precipitates at 1150 C.

Interstitial impurities were also thought to influence the swelling observed in ion-irradiated niobium subjected to sequential temperature changes during irradiation. Loomis and Gerber (206) found that the swelling was lower in material subjected to this irradiation procedure compared to the combined swelling expected from the separate isothermal irradiations. Both void shrinkage and void-growth effects occurred with the exact pattern of behavior depending on the precise temperature changes involved. Mechanisms based on the segregation of oxygen to the vicinity of void surfaces were postulated to explain the observed behavior whereby the neutral nature of the void was progressively altered by the oxygen arriving at the void surface.

In a series of niobium oxygen alloys, Loomis and co-workers (204) determined that the oxygen influenced the void size and density by rather an unusual mechanism. In the unirradiated **Nb-0** alloys, a population of small voids and void-shell composites were found which must have been formed during the elecron-beam zone refining used to purify the niobium. The void number density in the irradiated alloys was found to be related to the density of the small void and void shell composites observed in the unirradiated alloys.

In all the previous ion irradiations, no additional gas was introduced to stabilize the void populations. In a series of experiments, Loomis and Gerber (203) investigated the effect of simultaneous implantation of 0.87 MeV ${}^{3}_{\text{He}}$ on the void swelling in niobium and Nb-0.4 at percent oxygen alloy. The data presented in Table XXXVIII demonstrates that effect of up to 0.1 at percent helium only had a significant effect in pure niobium irradiated at 787 C. However, the authors noted a tendency to develop a bi-modal distribution of void/cavity sizes.

Nb-base alloys

a. Nb-12r. The temperature dependence of the void swelling and dislocation parameters for Nb-12r irradiated with 3.5 MeV Ni ions to 35-70 dpa at temperatures between 600-1150 C have been determined by Loomis and Gerber (201). The results adjusted to a dose of 50 dpa (Figures 30, 31) follow a similar pattern to the results in pure niobium discussed above although the swelling is slightly higher in the alloy than in the pure metal.

b. Nb-Ti, Ni, Mo and Fe Binary Alloys. Loomis and Gerber (205) have recently extended their work to simple binary alloys and a Nb-Mo-Hf ternary alloy and presented a most interesting study of the effect of different alloying elements on the void swelling produced by Ni⁺ ion irradiation. They employed both 3.0MeV Ni ion irradiation and simultaneous 3.0MeV Ni⁺ ion and .87 MeV 3He⁺ ion irradiation to produce displacement doses close to 50 dpa. The results given in Table XXXIX show that the simultaneous irradiation with ³He⁺ ions did not significantly change the swelling. From a comparison of the swelling obtained in the different alloys with values of solute diffusivity, relative chemical affinity, and lattice constant for the alloys



Figure 28. Plot of the temperature dependence of void swelling $\Delta V/V$ in niobium irradiated with 3.0 MeV Ni+ icms. Data adjusted to 50 dpa (201).



Figure 29. Plot of the temperature dependence of the number density and mean size of the dislocation loops and black spot damage in niobium irradiated with 3.0 MeV N1 ions. Data adjusted to 50 dpa (201).



Figure 30. Plot of the temperature dependence of the void swelling in Nb-1Zr irradiated with 3.0 MeV Ni ions. Data adjusted to 50 50 dpa (201).



IRRADIATION TEMPERATURE (°C)

Figure 31. Plot of the temperature dependence of the number density and mean size of the dislocation loop and black spot damage in Nb-12r irradiated with 3.0 MeV N1 ions. Data adjusted to 50 dpa (201).

	with 3.0 Me	⁵⁸ Ni ⁺ ions	or with 3.0 Me	ay 58 _{N1} + and	
	<u>0.87</u> Me	eV He ions	(0.002 at % He	<u>/dpa)</u>	
<u>A11oy</u>	Lon	Temp. (¢)	Damage (dpa)	He (at %)	<u>5 1/1</u>
Nb	^{нт} +	787	49	0	0.006
Nb	№1 ⁺ + Не ⁺	787	54	0.108	0.056
Nb	N1 ⁺	922	49	0	0.034
No	ы ⁺ + не ⁺	927	54	0.108	0.040
Nb + 0.4 at	N1 ⁺ % 0	787	47	0	0.007
Nb + 0.4 at	№1 ⁺ + Не ⁺ %0	787	51	0.102	0.008
Nb + 0.4 at	№1 ⁺ % О	937	43	0	0.049
Nb + 0.4 at	Ni+ + He ⁺ % 0	952	42	0.104	0.049

Table XXXVIII. Void Parameters for Nb and Nb 0.4 at % 0 irradiated

 $\frac{\text{Table XXXIX. Void and cavity parameters in Nb alloys irradiated}}{\text{with 30Mev}^{58}\text{N1}^{+}\text{ ions or 3.0Mev}^{58}\text{N1}^{+}\text{ ions and 0.87 MeV}^{3}\text{He}^{+}\text{ ions.}}$

Alloy	Lon	Tempera- ture (K) C	Damage (dpa)	Не (a/o)	Void Volume fractions (a/s)
Nb	Ni+	922	49	0	3.4
Nb + 2.2 a/o Ni	N1 ⁺	1210	45	0	2.3
Nb + 2.2 a/o Ni	Ni+ $+$ He ⁺	1195	44	0.088	1.2
Nb + 2.5 a/o Ti	÷1	1215	39	0	<0.1
Nb + 2.5 a/o Ti	₩ 1⁺ + He+	1205	48	0.096	0.2
No + 2.3 a/o Mo	+ i ⁺	1225	46	0	<0. 1
Nb + 2.3 a/o Mo	мі ⁺ + 8е ⁺	1225	47	0.094	0.1
Nb + 2.5 a/o Mo +	N1 ⁺	1220	46	0	<0. 1
2.5 a/o Hf					
Nb + 2.5 a/o Mo +	$\aleph_1^+ + He^+$	1220	49	0.098	<0.1
2.5 a/o Hf					
Nb + 2.3 a/o Fe	+1H	1225	48	0	2.1

the authors suggested that (i) the substitutional solutes nickel and ion that diffuse abnormally fast in niobium have a minor effect on the void $\Delta V/V$, (ii) the substitutional solute molybdenum, that diffuses abnormally slowly in niobium causes a significant reduction in $\Delta V/V$, (iii) titanium which has a strong affinity for oxygen causes a significant reduction in $\Delta V/V$. Loomis and Gerber (207) have also established that the low swelling of Nb-Ti alloys is retained at high levels of titanium (< 25 at %) at both 1050 K and 1250 K

<u>Void Lattice</u>. In ion-irradiated niobium and Nb-12r ordered arrays of voids oriented parallel to the host metal lattice, e.g. bcc, have been observed by both Brimhall and Kulcxinski (202) and Loomis and co-workers (203). Brimhall and Kulcxinski (202) found that the void lattice was not as well defined at 900 C as at 800 C 2nd that the ordering of voids first occurred after 60 dpa and was fairly well developed by 90 dpa. Loomis et al (203) established the important result that ordered void arrays were only formed in niobium and Nb-12r if the oxygen impurity concentration exceeded a threshold level. The threshold concentration was between 60 and 400 at. ppm for niobium and between 400 and 2700 at. ppm for Nb-12r. The ordering of the voids occurred at a low dose (<5 dpa) and the void lattice parameters were again very sensitive to irradiation temperature with the greatest degree of perfection occurring at 780 C and 800 C.

Loomis and Gerber (203) presented empirical and theoretical equations for the relationship between the void lattice parameters irradiation temperature, and oxygen-impurity concentration and suggested that the void spacing in ordered arrays is basically due to interstitial solute segregation to void surfaces.

Mechanical Properties

In this section the effect of irradiation on the mechanical properties of polycrystalline niobium and niobium base alloys will be considered. As one might expect, the very small penetration of energetic charged particles makes mechanical testing of irradiated samples difficult, although alpha particle irradiations have been employed to study the effect on the mechanical properties of the high helium concentrations typical of a fusion reactor (see section "Effect of Helium on Mechanical Properties"). Most attention has been given to the effect of fast neutron irradiation on the mechanical properties, as it is obviously simple to irradiate the comparatively large volumes of material required for mechanical testing. This data will be reviewed below.

Effect of fast neutron irradiation. The majority of studies using neutrons have employed post-irradiation tensile testing of irradiated test pieces. The data on niobium covers a wide variety of microstructures, temperatures and fluences, while only restricted information is available on niobium alloys. Nb-12r and Cb-752 are the only alloys on which data was found. In Table XL a representative selection of data is given on the effect of irradiation on the strength and ductility as measured by post-irradiation testing (190, 209-213). In all the cases the effect of the irradiation was to strengthen the material, with the magnitude of the increase dependent on the irradiation temperature and fluence. Accompanying this increase in strength was a loss of ductility particularly of uniform elongation, which may approach zero (211-212). However, even in the latter case, the total elongation remained high. The data obtained by Wiffen (211) at high doses demonstrate that alloying with 1 percent zirconium produced a greater increase in stength but a greater reduction in uniform ductility than in niobium irradiated and tested under similar conditions. The other notable

Makandal	Fast Fluence n/m ²	Irradiation	Test	0.2 Yiel Stren (MP:	ld ngth a)	Ultin Tens Stren (MP	nate sile ngth a)	Unife	Elonga	tion Z Tota	1	Reduc	tion
Material	<u>~ 1 nev</u>		<u>(</u>	UNITT	<u>111</u>	ORIFT	<u>1rr</u>	LIALTE	TLE	INDIFE	ITT	<u>in ar</u>	ea X
	9.1 × 10	17	RT	134.5	293	276	319	-	-	51.5	415		
	9.1 X (0	17	RT	110	281	240	292	-	-	53.0	38.5		
Nb (00.0¥)	9.7 × 10	17	RT	119	205	240	314	-	-	53.0	31.5		
(99.84)	9.7 × 10	17	RT	148	285	201	297	-	-	45.0	32.9		
(209)	9.7 × 10	330	RT.	134		210	384	-	-	51.5	21.8		
	9.1 X IU	330	RT	134	317	270	301	-	-	-	-		
	9.1 x 10 ²¹	330	RT	134	-	216	319	-	-	50.0	31.4		
	9.1 x 10 ²¹	330	RT	134 134	302	276 276	328 305	-	-	45.0 45.0	24.3 20.8		
	/ x 10 ²⁴	125-175	RT	410	532	495	554	-	-	20.6	8.0		
	1 x 10 ²⁴	125-175	RT	410	511	495	513	-	-	20.6	6.4		
Nb	/ x 10 ²⁴	125-175	RT	410	513	495	531	-	-	20.6	6.5		
(210)	× 10 ²⁴	125-175	RT	410	636	495	640	-	-	20.6	6.8		
	1 x 10 ²⁴	125-175	RT	410	636	495	639	-	-	20.6	7.1		
	1 x 10 ²⁴	125-175	RT	410	629	495	632	-	-	20.6	4.2		
	3 x 10 ²⁶	460	25	110	430	210	528	27	10	60	17	95	71
Nb ^(a)	3.1 × 10 ²⁶	440	400	12	343	174	411	25	1	39	15	92	85
(211)	3×10^{26}	460	400	72	394	174	441	25	5	39	13	92	85
	3 x 10 ²⁶	460	650	60	326	121	348	22	3	41	12	91	47
	8.8 x 10 ²³	50 C	RT	380	401	412	433	3.2	0.5			19	69
	8.8 x 10 ²³	50 C	RT	380	432	412	445	3.2	0.6			79	12
Nb-12r	1×10^{24}	50 C	RT	380	430	412	448	3.2	0.6			79	12
(212)	/ x 10 ²⁴	50 C	RT	380	434	412	443	3.2	0.5			19	55
	1.5 x 10 ²⁴	50 C	RT	380	423	412	439	3.2	0.6			79	12
	1.5 x 10 ²⁴	50 C	RT	380	445	412	450	3.2	0.6			79	81
	1.9 × 10 ²⁶	394	25	112	563	221	614	30	3	52	12	94	82
Nb-1Zr ^(a)	3.1 x 10 ²⁶	448	25	112	638	221	638	30	0.1	52	9	94	89
(211)	1.9 x 10 ²⁰	394	400	122	499	113	499		0.1	28	9	95	74
	3.1 x 10 ²⁶	448	400	122	512	173	512		0.1	28	9	95	85
(a) >0.	3.1 × 10 ²⁶ lMeV	448	650	85	451	186	451		0.1	24	9	80	83

Table XL (A). Effect of fission neutron irradiation on the mechanical properties of Nb and Nb-1Zr.

feature of the Nb-l2r results was that the maximum load was reached within 0.2 percent deviation from the elastic modulus line, and thus the measured yield strength and ultimate tensile strength were identical. This contrasted with behavior of pure niobium and is illustrated in Figure 32 for a test temperature of 400 C.

At low doses (< 10^{24} n/m²) there have been several attempts to correlate the changes in the mechanical properties with the observed microstructure. Loomis and Gerber (192) in a study of niobium containing oxygen considered that the increase in the resolved shear stress could be correlated with the density and diameter of the irradiation induced defect clusters. However, more recently Kayamo and Yajima (214) suggested that discrepancies they found between the athermal components of the yield stress and the stresses derived from the observed defect distributions were due to interactions between interstitial impurities and radiation-produced defects. Loomis and Gerber (172) also suggested that impurity atom-irradiation produced defect complexes that were not resolvable in the electron microscope were contributing to the hardening at doses below 3 x 10^{21} n/m².

The effect of neutron energy has been investigated by Mitchell et al (218) who compared the radiation strengthening produced in Nb by fusion and fission neutrons at doses < $10^{22} n/m^2$. The authors found that fusion neutrons produced greater strengthening, both when the data was compared on the basis of neutron dose and of damage energy.

Effect of helium on mechanical properties. As described in the section "Neutron interactions with niobium", one of the major differences between the irradiation response of a structural material in fission and fusion neutron irradiations is in the significantly greater amount of helium generated by fusion neutrons. This has considerable practical implications as it is well established that the formation of helium bubbles has a very important influence on mechanical properties, particularly on the fracture mode at elevated temperatures. The influence of helium on the mechanical properties of both niobium and Nb-12r have been studied by a variety of techniques including alpha particle bombardment and tritium decay.

Atteridge et al (216) and Baramore et al (134) have studied the effect of high helium concentrations on the mechanical properties of niobium. The high concentrations were introduced by diffusing tritium in to suitable specimens and allowing this to decay to helium, and then removing the remaining tritium by an appropriate heat treatment in vacuum. In this manner, concentrations of between 25 and 500 appm were achieved. The main conclusions from these studies are that for a wide range of helium concentrations, the material is not strengthened at room temperature (134) but that strengthening does occur at elevated temperatures without a severe loss of ductility (215, 216). The latter trend is illustrated in Figure 33 where the results of Baramore et al at 800 C and Atteridge et al at 1020 C are presented. Baramore et al considered that the greater strengthening observed by Atteridge et al in their helium containing specimens was due to a greater degree of helium agglomeration in the material during thermal processing of the tritated specimens. Similar trends were observed at the lower strain rates employed in creep tests. Baramore et al (134) found that at temperatures between 700 and 1000 C the steady state creep rate and strain to fracture decreased progressively with helium content, indicating the material strengthened but with an attendent loss of ductility. The strengthening effect of the helium was attributed to the combined effects of dislocation/helium-bubble interactions, and grain-boundary hardening by helium bubbles.



Figure 32. Tensile curves for irradiated Nb~1 % Zr (3.7 x 10^{26} n/m² at 450 C) and Nb (3.0 x 10^{26} n/m² at 460 C) tested at 650 at 0.02 min⁻¹ (211).



Figure 33. Effect of helium concentration on yield and ultimate stress and elongation of niobium tested at 1020 C at 0.02 min^{-1} (216) and at 800 C (215).

From the dependence of the uniform elongation and strain-hardening on helium content, Atteridge et al (216) deduced that a change in the dominant mode of deformation occurred at high helium levels. They had observed that the uniform elongation decreased continuously until 250 appm helium and then dropped sharply. This coincided with a change in the stress-strain behavior, at >250 appm helium the strain hardening after yield found at lower concentrations was not observed. The authors interpreted this behavior as indicating that plastic deformation within the grains was the dominant mode of deformation at $\langle 250$ appm helium but that grain boundary sliding become important at higher concentrations. Indeed grain boundary decohesion was present in the necked region of specimens containing 500 appm helium.

The effect of helium on the mechanical properties of niobium base alloys has only been studied in Nb-IZr implanted with alpha particles. Wiffen (219)studied the effect of 50MeV alpha particles bombardment at room temperature to gas contents of 2 to 20 appm helium on the elevated temperature properties of Nb-12r. Tensile tests at 1000 C and 1200 C showed no significant effect of helium. Creep rupture ductility measurements at the same temperature showed some reduction of ductility in the helium injected samples. However, the lack of dependence on helium content, an apparently smaller effect at 1200 C than at 1000 C, and the absence of the classical features associated with helium embrittlement in microstructural examination was taken to indicate that the reduction in creep ductility was dependent on another mechanism. The observed precipitate phases suggested that the embrittlement was due to oxygen pick-up during the implantation. It was concluded that helium contents of up to 18 appm did not significantly degrade the properties of Nb^{-} [Zr at above 1000 C. From the results of tensile tests at lower temperatures, 20 to 800 C, Saques and Auer (219) similarly concluded that the ductility of Nb-12r was not significantly affected by up to 80 at. ppm of helium implanted using a 100 MeV alpha particle beam at 50 C and 600 C.

Helium bubble behavior in niobium and niobium-zirconium alloys. Tt is clear from the discussion above that helium bubble nucleation and growth is important in determining the mechanical behavior of niobium. Goodhew and coworkers (220-227) have studied helium bubble growth by migration and coalesence in several bcc metals including niobium and niobium zirconium alloys. They demonstated that the rate limiting process controlling the bubble growth depended sensitively on both bubble size and the composition of the bubble surface. The experimental procedure consisted of nucleating bubbles in the grain interior (within 200-800nm of the surface) and studying their growth under isothermal conditions. They also extended existing theoretical models to include both the possibility that nucleation of a surface ledge may control the migration rate of faceted bubbles, and that the condition of constant gas pressure in the bubbles may apply at low temperatures (227). From a detailed comparison of the experimental growth rates and the behavior predicted by the theoretical models, they were able to show that the observations were consistent with bubble migration by a surface diffusion mechanism. In pure niobium, the rate limiting process was shown to be surface diffusion for small bubbles but ledge nucleation for large bubbles. The latter gave rise to very low growth rates and a cessation of bubble growth effectively occurred over the temperature range studied (950-1250 C). The bubble growth behavior was more complex in niobium-zirconium alloys. The observations were consistent with the zirconium causing changes in the ledge energy as the isothermal anneal proceeded. Initially the addition of zirconium cleansed the bubble faces of oxygen which had the effect of increasing the ledge energy. At longer times the segregation of Zr-0 complexes to the bubbles further altered the ledge energy. The ledge energies deduced from the quantitative modelling are given in Table XLI. It is to be emphasized that
the bubble size at which the growth is controlled by ledge nucleation was found to depend sensitively on the ledge energy, increasing sharply with decreasing ledge energy. For example, in Nb-12r annealed at 1050 C, the decrease in the ledge energy from $11 \times 10^{-11} \text{ J/m}$ to $4 \ 10^{-11} \text{ J/m}$ increased the bubble size from 2nm to 5nm.

Table XLI. Ledge energies on	the (100) face of niobium
determined by Goodhew and Tyler.	
Pure Niobium	- 11 x 10 ⁻¹¹ J/M
Niobium containing 400/10 ⁶ oxygen	$\sim 1.2 \text{ x } 10^{-11} \text{ J/M}$
After segregation of Zr-0 to the surfaces	$\sim 4 \times 10^{-11} \text{ J/M}$

Clearly, under the conditions investigated by Goodhew and co-workers, there is no displacement damage or helium generation occurring during the growth of the bubble population. This limits the application of their results to an irradiation environment but Goodhew and Tyler (227) point out that if during irradiation at high temperatures bubbles are mobile then any segregation to internal surface induced by the irradiation could modify bubble mobility dramatically.

Summary of Irradiation behavior

In the section "Neutron interactions with niobium" it was shown that the interaction of niobium with fast and thermal neutrons has been well described in the literature. As in other metals, the various cross-sections are dependent on neutron energy. The absorption cross-sections are low for thermal neutrons in comparison with other elements, but are high for 100keV neutrons. The latter presents a barrier for the use of niobium base alloys in a fast reactor. The energy dependent neutron collision cross-sections are sufficiently well established for the recoil spectra created in different neutron sources to be reliably calculated. The recoil spectra show the expected dependence on neutron energy with high energy recoils being created by fusion neutrons. Niobium alloys have been considered as possible containment materials for fusion reactors and it was shown that the transmutation gas production (H. He) in niobium is lower than in other possible structural materials. However, the long lived activity of Nb gives an unacceptably high level of activity over the long term. Although this was considered in the context of a fusion reactor, it is equally a drawback to the use of niobium in fission reactors.

Surface effects, particularly blistering, have received more attention than any other irradiation induced phenomena. These studies, primarily with monoenergetic He and H **ions** have established the dependence **on** material and irradiaion parameters. They have **also** been important in the examination of the mechanisms underlying blistering. It is perhaps surprising that there have been relatively few studies on niobium alloys.

The studies on the microstructure generated under neutron irradiation have shown that the development of the microstructure follows the pattern established in other metals. At low doses, a uniform distribution of small defects clusters are created, the size and density of which depends on the precise irradiation parameters and the purity of the material. At high doses a more complex microstructure evolves consisting of network dislocations, dislocation loops and voids. The void swelling values reported for niobium show some variation, possibly due to different purity material being used. The swelling is thought to peak at 1000 C and the observed swelling is generally quite low, for example, only 1.5 percent swelling was observed at a dose of 21 dpa at 600 C. The void swelling is suppressed or reduced in alloys containing appreciable zirconium or molybdenum. Indeed in Nb-12r appreciable swelling has only been observed in a narrow temperature range around 790 C.

The extensive void swelling studies by Loomis and co-workers using ion irradiation have extended the range of parameters examined. Possibly the most important aspect of their work is identifying the important role played by interstitial impurities, and in particular, oxygen. They also deomonstrated that alloying elements that diffuse abnormally slowly, i.e. molybdenum or that have an affinity for oxygen, i.e. titanium, cause a significant reduction in swelling.

Post-irradiation tensile testing of neutron irradiated niobium and Nb-lZr have shown that the material is strengthened with the magnitude of the increase depending on the irradiation temperature and neutron fluence. This strengthening is accompanied by a dramatic decrease in uniform elongation although the total elongation remains at a tolerable level. Indeed in Nb-lZr the uniform elongation drops to near zero.

The effect of low levels of helium (<20 appm) has little effect on the mechanical properties of Nb-lZr. High levels of helium introduced by the tritium trick caused the material to strengthen at elevated temperatures without a severe **loss** of ductility. There was evidence the dominant mode of deformation at 1020 C was dependent on helium concentration. At concentrations <250 appm plastic deformation within the grains was the dominant deformation mode, but grain boundary sliding became important at higher concentrations.

It is apparent from the above that interstitial impurities play an important role in processes involving the diffusion or clustering of the irradiation produced point defects. Indeed point defect impurity trapping makes the study of the basic properties of the point defects very difficult. Oxygen has received the most attention, its role in the development of the microstructure at both high and low doses has been identified. It appears from the work of Loomis and co-workers to strongly influence void growth through its effect on the void surface. The interaction of oxygen with a bubble surface was also identified by Goodhew and co-workers as strongly influencing the rate limiting step in the growth of bubbles under isothermal conditions. It is interesting that whereas the nitrogen and carbon were found to strongly affect the mechanical properties of niobium, their role in affecting the irradiation response has not as yet been established.

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