FABRICATION OF NIOBIUM AND NIOBIUM ALLOYS

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Introduction

Fabrication of niobium and niobium alloys is accomplished with the usual metal forming methods and apparatus; however, the metallurgical engineer must design the deformation parameters within the plastic tolerance of the material being worked. Niobium has a wide plastic region so it is relatively insensitive to deformation paramenters. In contrast, niobium alloys have very narrow plastic regions within which the metallurgist must carfully plan the deformation parameters.

I will first discuss the material characteristics which are important to the metallurgist for planning the deformation parameters, and follow with descriptions of specific processes for the manufacture of niobium and alloys.

Nb Manufacture

Niobium melts at 2468 C, which is well above the melting point of most other materials. As a result, it is readily purified by melting in a vacuum of 5 x 10^{-5} torr, suitable for the evaporation of impurities from the metal.

The impurities which remain after electron beam melting are at low levels (<100 ppm), such that they are mostly soluble in pure niobium. The materials which do not dissolve, concentrate at the cast grain boundaries which, consequently, are the weakest sites; thus, fracture occurs when the grain boundaries are stressed beyond their ultimate strength.

Niobium is tough and ductile in the pure form and can be worked at ambient temperatures from the cast ingot. Any precautions that are necessary result from the residual impurities in the ingot since impurities which remain after the purification process cause a reduction of ductility, primarily at grain boundaries. Therefore, techniques to eliminate grain boundary fracture during deformation are necessary.

For pure niobium ingots, processing techniques are simple. Impurity content is determined by sample analysis, and the effect is demonstrated in a general way by the degree of hardening. Brinell hardness numbers (BHN) below 60 indicate that the ingot will not suffer fracture during deformation. Bardnesses higher than 60 BHN indicate that impurities are causing hardening and a corresponding ductility decrease. In such cases, it may be advisable to apply heat, up to 400 C, to provide for improved ductility of the hardened portions of the ingot (i.e. the grain boundaries).

Although niobium is soft and ductile, separations do not readily weld together and "heal" during ambient temperature forming. Instead, laps, folds, seams and laminations form where separations exist. Therefore, it is necessary to prepare the niobium for fabrication by machining or grinding to provide a smooth, well blended surface. If internal voids exist, they will appear as delaminated regions in the fabricated niobium, never totally healing, resulting in a weakened part.

Prior to any working operation, the niobium surface needs to be inspected closely for irregularities. Techniques include dye penetrant, ultrasonic, and x-ray inspection.

After initial ingot deformation of at least 65 percent cold reduction, a recrystallization heat treatment in the 10^{-5} torr vacuum range is advisable. The new grains will be refined from the cast structure, and the impurities originally located at the surface of the cast grain boundaries will be dispersed throughout the matrix as second phase stringers. This recrystallization will improve the resistance to grain boundary tearing during subsequent working, thereby improving fabricability.

For most applications, a uniform and fine recrystallized microstructure is beneficial. Pure niobium is sensitive to the time and temperature parameters applied, especially as the degree of purity increases. Residual impurities will act as inhibitors to recrystallization and grain growth. As the cast ingot hardnesses become greater than 60 BHN, response to annealing is sufficiently affected to require evaluation anneals in order to determine a time and temperature cycle which will provide uniform and fine recrystallization.

Niobium can recrystallize at temperatures as low as 1500 F (815 C), and may remain only partially recrystallized at 2200 F (1200 C). In addition to impurity content, the degree of deformation and the temperature of deformation effect the choice for optimum annealing cycle to achieve a uniform microstructure (Figure 1). As a general statement, a minimum of 65 percent ambient temperature deformation is required to achieve total nucleation of new grains during annealing. Warm or hot deformation operations (1000 F to 2000 F) (550 C to 1100 C) will produce a worked cross-section which varies sufficiently to produce a wide range of responses to the annealing cycle. The microstructure can exhibit nucleation of new grains in local bands of heavily worked metal, critical grain growth in bands of lightly worked metal, and regions of metal which remain stable and do not nucleate new grains or recover for critical grain growth.

Pure niobium is tough and malleable in most conditions. The fine and uniform microstructure is recommended primarily for forms which will be worked further or welded, because fine grains resist tearing and orange peeling associated with large grain boundary failure.

Alloys

Alloying niobium produces, in most cases, immediate and severe complications for the fabricator. The three exceptional alloying elements are titanium, vanadium and tantalum (Figures 2, 3, 4). Although hardness and strength are increased with these latter additions, toughnes, malleability, and fabricability are equal to or even superior to pure niobium. All other alloying elements reduce toughness, malleability, and fabricability in varying degrees.

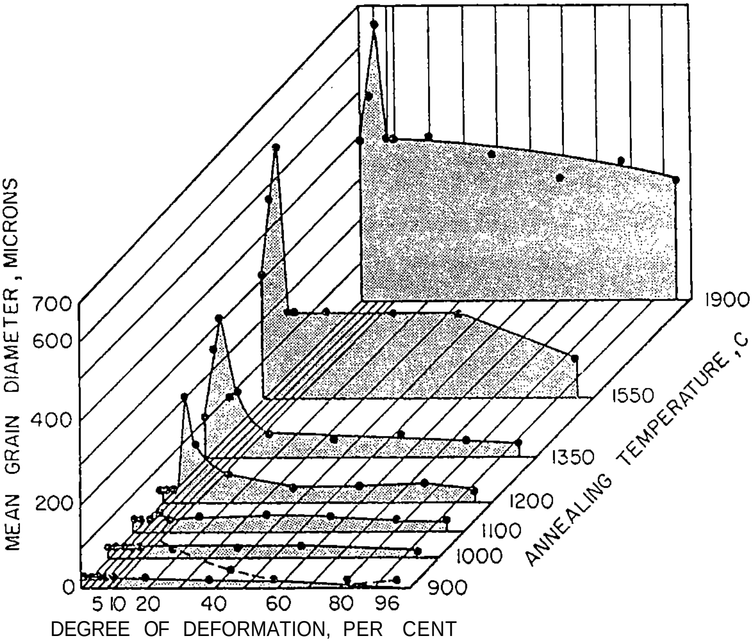
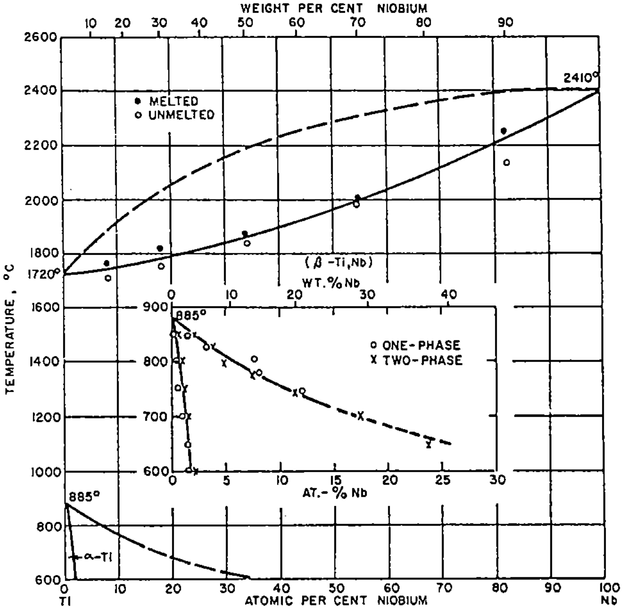
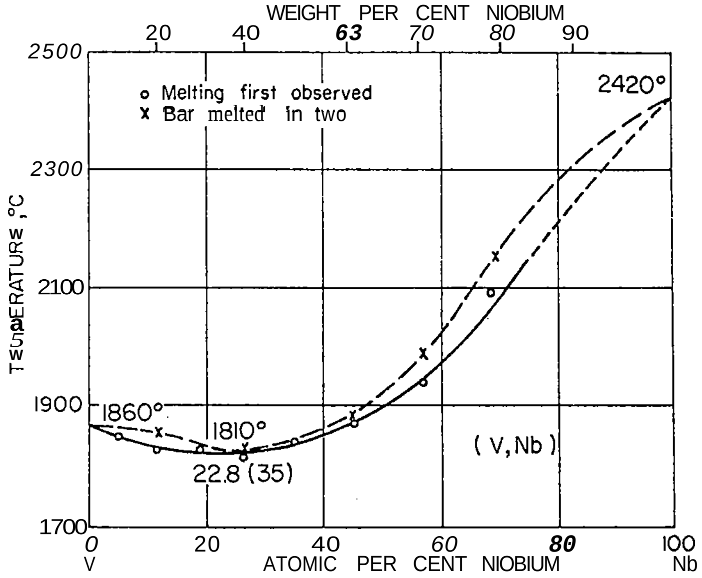


Figure 1. Annealing temperature versus deformation and grain size. (1)



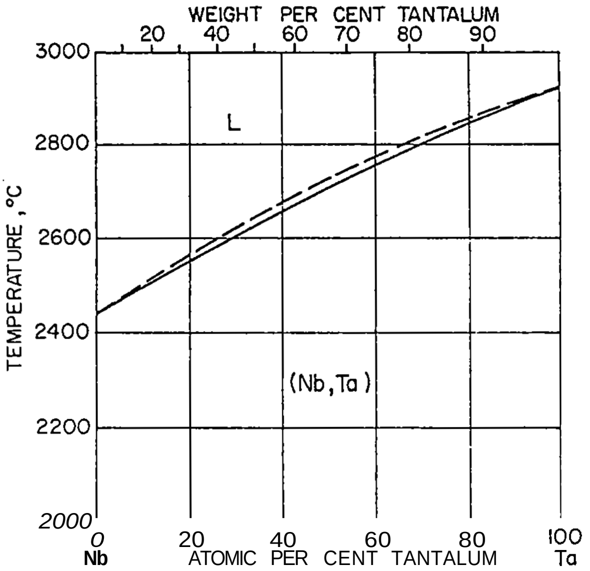
Nb-Ti

Figure 2. Phase Diagram Nb-Ti system. (2)



Nb-V

Figure 3. Phase Diagram Nb-V system. (2)



Nb-Ta

Figure 4. Phase Diagram Nb-Ta system. (3)

The simple binary, solid solution alloys containing either tantalum, vanadium or titanium provide an increase in fabrication difficulty only because of increased strength. Resistance to deformation of the stronger alloys usually requires the use of higher working temperatures so that deformation can be accommodated by the lower strength material.

Use of elevated temperatures provides the additional benefit of producing an increased number of deformation modes in the crystal structure, thus slowing work hardening rates. These benefits are important and may even be necessary with the simple binary alloys (NbV and NbTi) because other impurities are usually associated in large amounts with the alloying element. The impurities will alloy with the parent metal as an interstitial element or as complex compounds. Both the dissolved interstitial elements and the insoluble compounds produce dramatic hardness increases and the associated loss of ductility, even in amounts greater than 200 ppm for common impurities such as nitrogen, carbon, iron, nickel, copper and aluminum.

The exceptional malleability of these simple binary alloys results in tolerance for large amounts of impurities once the cast ingot has been processed through a 65 percent minimum deformation and recrystallization operation. Refining the grains and distributing the bulk of impurities away from the grain boundaries is increasingly important for recovery of excellent malleability as the total impurity level increases. A discussion of the effects of each possible impurity and the effects of the total amounts of impurities is beyond the scope of this paper. In general, the specifications developed by suppliers such as Teledyne Wah Chang Albany for each alloy have been demonstrated to be suitable for most uses, and certainly for economical fabricability (Tables I, II, III).

Complex niobium alloys always provide continuing challenges for the metallurgical engineer. These alloys contain the alloying additions which

Table I. Suppliers' Specifications for Commercial Nb Alloys.

Element	Nb Grade I	Nb Grade II	WC103	WC129Y	Nb-1Zr	Nb-752
Tungsten	500*	500*	5000*	9-11 %	500*	9-11 %
Hafnium	---	---	9-11 %	9-11 %	200*	2000"
Tantalum	1000"	3000*	5000*	5000*	1000"	5000*
Yttrium	---	---	---	.05-.3%	---	---
Titanium	---	---	.7-1.3%	---	---	---
Zirconium	500*	500*	7000*	5000*	.8-1.2%	2.0-3.0%
Carbon	100*	100*	150*	150*	200*	150*
Oxygen	200"	200"	250*	225*	300*	225*
Nitrogen	100"	100"	100*	100*	100"	100"
Hydrogen	15*	15*	15*	15*	15*	15*
Niobium	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

"Maximum limits unless otherwise indicated. *ppm - Parts Per Million

3.2.1 Product analysis. If specified, product analysis shall be performed on C, O_2, N with maximum levels specified as follows on Parts Per Million (ppm).

Element	Nb	WC103	WC129Y	Nb-1Zr	Nb-752
C	100	150	150	200	150
O_2	200	225	225	300	225
N	100	100	100	100	100
H	15	15	15	15	15

Table 11. Suppliers' Specifications for Nb-Ti Superconducting Alloys.

Chemical Composition SUPERCONDUCTOR ALLOY

Melt The chemical composition shall be as follows:

Ti	45, 46.5, 48, 55 wt% ± 1.5 wt% *
O	1000 ppm maximum
H	35 ppm maximum
C	200 ppm maximum
Fe	200 ppm maximum
Ta	1000 or 2500 ppm maximum *
N	150 ppm maximum
Ni	100 ppm maximum
Si	100 ppm maximum
Cu	100 ppm maximum
Al	100 ppm maximum
Cr	60 ppm maximum
Nb	Balance

*To be determined at a later date. (see purchase order)

Niobium or titanium may be analyzed, with the other element reported as balance by difference.

Finished Product Chemical analysis of the finished vacuum annealed product shall be performed for the interstitial elements and shall conform to the following limits:

O	1000 ppm maximum
H	20 ppm maximum
C	200 ppm maximum
N	150 ppm maximum

Table III. Suppliers' Specifications for Nb based Refractory Alloys.

Chemical Composition *

Element	MT1-5-1 (Nb-10 Hf-1 Ti)	MT1-5-2 (Nb-10W-10 Hf-.2Y)	MT1-5-3 (Nb-10W-10 Ta)
Tungsten	0.5 wt. %	9-11 wt. %	9-11.5 wt. %
Hafnium	9-11 wt. %	9-11 wt. %	1000 ppm **
Tantalum	0.5 wt. %	0.5 wt. %	9-11.5 wt. %
Yttrium	-	0.1-0.4 wt. %	-
Titanium	0.7-1.3 wt. %	100 ppm	100 ppm
Zirconium	0.7 wt. %	0.5 wt. %	0.5 wt. %
Carbon	150 ppm	150 ppm	150 ppm
Oxygen	225 ppm	225 ppm	225 ppm
Nitrogen	150 ppm	150 ppm	150 ppm
Hydrogen	15 ppm	15 ppm	15 ppm
Boron) Cadmium) Cobalt) Iron) Lead) Manganese) Molybdenum) Nickel) Silicon) Vanadium) All others)	3000 ppm Total	3000 ppm Total	3000 ppm Total
Niobium	Balance	Balance	Balance

* Maximum limits unless otherwise indicated.
** ppm - parts per million

form complex compounds and phases, producing great strengths at elevated temperatures and significant reductions of ductility at ambient temperatures. The alloying elements generally recognized as suitable for commercial alloys are those which are soluble up to 10 percent by weight or greater. These include zirconium, hafnium, tungsten and molybdenum (Figures 5, 6, 7) as well as tantalum, vanadium and titanium. The stable compound formers, carbon and nitrogen, may be added in conjunction with titanium, zirconium, or hafnium to provide additional strength and creep resistance at elevated temperatures. In general, for each benefit realized by enriching the alloy, another benefit is compromised, especially weldability and toughness.

The complex alloys display the great strength at elevated temperatures which makes them attractive industrial materials. This strength benefit introduces an immediate challenge of fabrication from the cast state. The cast grain boundaries are extremely weak at ambient temperatures, so hot fabrication at 1800 F (975 C) to 2600 F (1425 C) is required.

Malleability is extremely poor in the casting for the complex alloys, so metal flow must be controlled during breakdown to avoid fracture by a mode best described as tearing. A good analogy to these cast materials is clay: clay can be gently worked and shaped, but a sudden pull will tear the material apart. In the same manner, complex niobium alloys will tear apart, crack or rupture when work is applied with either too great a severity (high energy rate deformation), or too slight (press forging). The high energy rate impact overloads weaken regions such as grain boundaries faster than the deformation wave can move through the metal, and consequently, these regions split apart. Slow deformation only works the surface and provides inadequate energy to move a deformation wave through the metal in a uniform transition. The worked surface thus develops a tensile load on the center portion, causing a rupture, or center burst.

The optimum breakdown operation for cast ingots is a compression method, usually extrusion. When the material is under compression, rate of deformation is important only in terms of maintaining temperature in the material for sufficient time to complete the operation.

Manufacture of Niobium/Niobium-Tantalum products - Outline

1. Warm the cast ingot to 400 F to 800 F.

2. Forge to reduce the cross section as desired, including:

   a. 2000 ton press forge
   b. 7500 lb. steam hammer
   c. Extrusion press
   d. Rotary forge

3. After 65 percent minimum to 85 percent reduction in cross sectional area, clean and anneal in 10^{-5} TORR vacuum at 2000 F for 1 hour.

4. Further reduce the material at ambient temperature as desired:

   a. Rolling, plate or rod
   b. Swaging
   c. Rocking
   d. Drawing, tube or rod

5. After 65 percent to 95 percent cold reduction, anneal at 1600 F to 2200 F to achieve desired grain size and hardness.

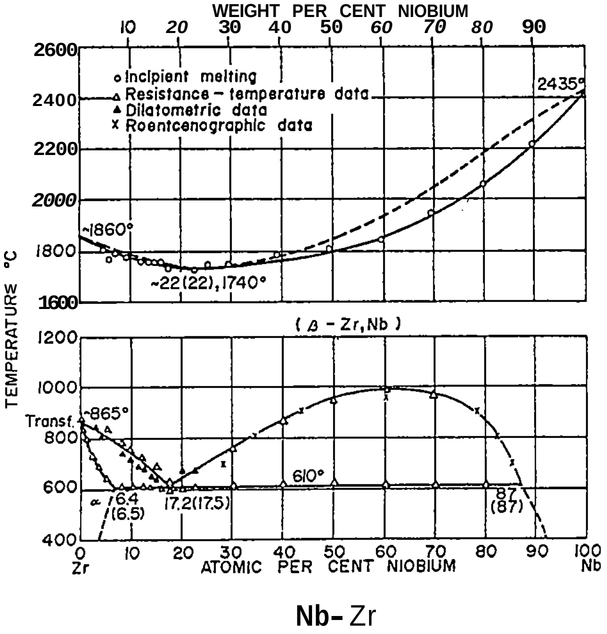


Figure 5. Phase Diagram Nb-Zr system. (2)

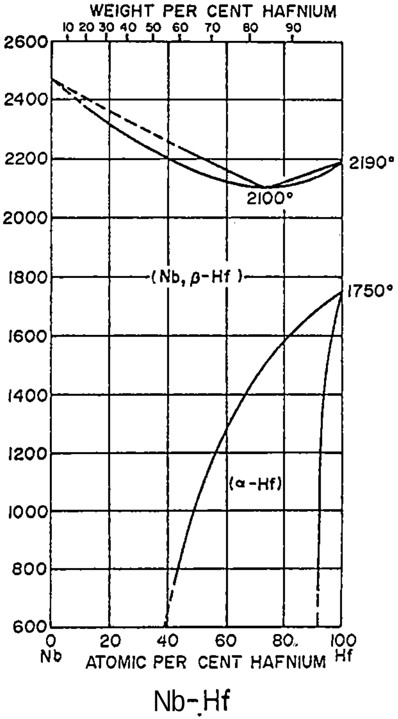


Figure 6. Phase Diagram Nb-Hf system. (4)

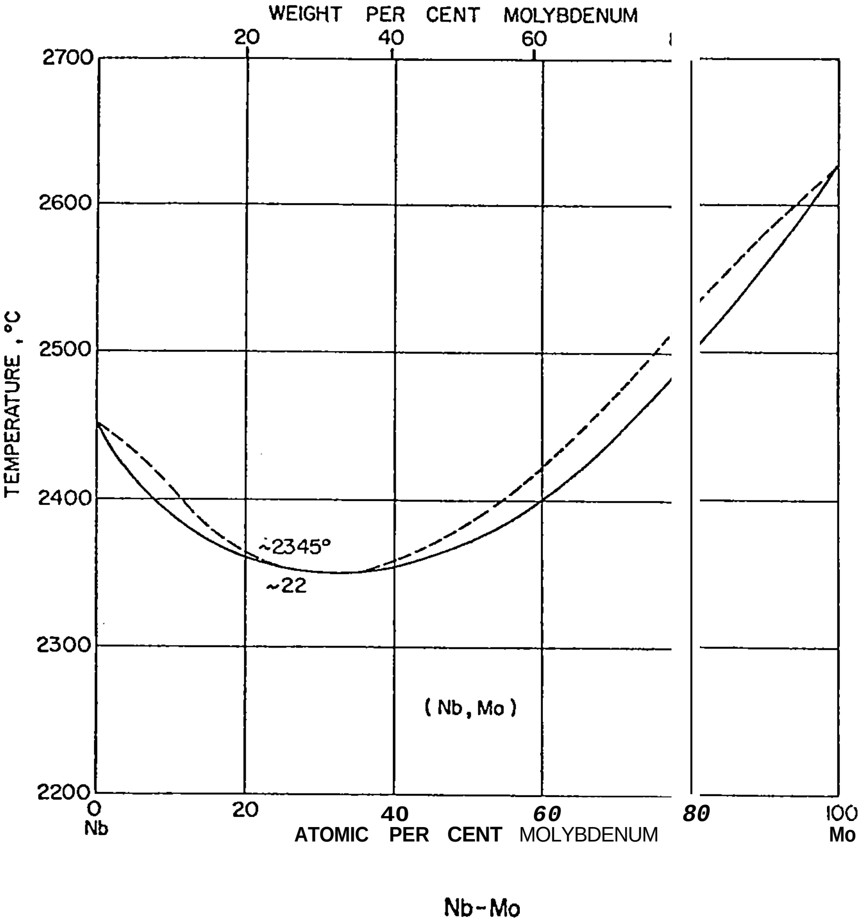


Figure 7. Phase Diagram Nb-Mo system. (3)

Manufacture of Niobium–Titanium - Outline

1. Warm the cast ingot to 2000 F.
2. Forge like pure niobium, 65 percent to 85 percent reduction.
3. Mechanically and chemically remove oxides and embedded matter from the surface.
4. Air anneal at 1750 F and water quench.
5. Warm forge or extrude (1250 F) to 65 percent minimum reduction.
6. Mechanically and chemically clean for vacuum anneal.
7. Vacuum anneal in 10^{-5} TORR at 1450 F for 1 to 2 hours.
8. Further work at ambient temperature to desired configuration.
9. Vacuum anneal to achieve desired grain size and hardness.

The only differences between techniques for forming niobium and niobium-titanium are the use of elevated temperature to deform the niobium–titanium alloy, and a quench from anneal for the niobium–titanium because of the Alpha to Beta phase transformation (Figure 2).

Forming the high strength alloys requires careful consideration at each operation to minimize fracture. The strength of the alloys at elevated temperatures (Table IV) places constraints on the equipment which has capacity for imparting work to the given alloy. Because the. first criterion calls for imparting work into the cast structure and compressive deformation is the most tolerant working mode, closed die forming is preferred for the initial breakdown. An extrusion press with a 5000 ton capacity and an extrusion rate of 30 inches per minute is often necessary to accomplish ingot breakdown. An example of the manufacturing outline follows:

Manufacture of Cb-10Hf-10W - Outline

1. Heat to 2400 F (1315 C).
2. Extrude from 8 inch diameter to 3 inch diameter at 30 inches per minute ram speed.
3. Machine all surfaces to remove oxide.
4. Vacuum anneal at 2600 F (1425 C) for 2 hours.
5. Heat to 800 F (425 C) and rotary forge to 1-1/2 inch diameter.
6. Vacuum anneal at 2400 F (1135 C) for 2 hours.
7. Swage at 400–600 F (200–300 C) to desired diameter.

Table IV. Mechanical Properties of Niobium and Niobium Alloys.

	UTS (ksi)	UTS (ksi)	Elong. %
Nb (RT)	25-35	11-20	35-45
Nb-1Zr (RT)	35-45	15-25	20-30
(800 F)	25	12	20
(2000 F)	20	9	40
Nb-10Hf-1Ti (RT)	54-64	38-50	20-30
(WC-103) (1000 F)	46	30	20
(2000 F)	29	19	40
Nb-10Hf-10W (RT)	80-90	60-70	20-30
(WC-129Y) (1000 F)	59	39	18
(2000 F)	42	25	40

Summary

Niobium, niobium-tantalum, niobium-vanadium and niobium-titanium metal and alloys are readily fabricated using standard techniques for deformation. The primary design considerations are the metallurgical structure, grain size, uniformity, and for niobium-titanium alloys the alpha-beta phase transformation.

For the alloys designed for improved strength at elevated temperatures, an associated reduction of ductility requires the use of high temperatures and compressive modes of deformation to refine the cast structure. Fracture sensitivity decreases (i.e., toughness improves) after the cast structure is worked and refined to provide greater grain boundary area which is lower in impurity phase decoration then the cast structure.

The material cost for niobium and the alloys is high, so that the success of the metallurgist in applying sound manufacturing techniques is important. With careful metallurgical consideration and close monitoring of each operation, niobium and the alloys can be successfully processed.

References

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