

THERMOMECHANICAL PROCESSING AND PROPERTIES OF NIOBIUM ALLOYS

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Abstract

Of all the refractory metals, which have melting points above 2000°C , niobium alloys are the most fabricable and lowest density. Niobium alloys are utilized in applications ranging from communication satellites to human body imaging equipment, yet most scientists and engineers have only limited experience with these materials. Over 95% of all niobium is used as alloy additions in steel and nickel alloys. Only 1-2% of niobium is used in the form of niobium-base alloys or pure niobium metal. Of this small percentage, superconducting niobium-titanium alloy accounts for over one-half of all niobium alloys produced. The remaining usage of niobium is for high temperature niobium alloys and corrosion applications. All of the high-temperature niobium alloys in use today were developed in the 1960s (1-3) for nuclear and aerospace applications. Compared to other refractory metals and the hundreds of refractory alloys investigated in the 1960s - 1970s, commercial niobium alloys are relatively low-strength but they are extremely ductile and can be fabricated into very complex shapes. Even though niobium alloys have useful strength hundreds of degrees above nickel-base superalloys, their use has been limited by oxidation and long-term creep behavior. This paper presents a brief view of how niobium alloys are manufactured today and a summary of their thermomechanical properties.

Ingot Production Methods

Since the early 1960s, crude niobium metal has been produced by aluminothermic reduction and then purified by electron beam melting. In aluminothermic reduction, Nb_2O_5 and aluminum powders are blended together and then reacted exothermically to form crude niobium metal and Al_2O_3 slag. The crude niobium metal typically contains several percent impurities, including primarily aluminum and oxygen. These impurities (Al , Al_2O_3 and Nb sub oxides) have a much higher vapor pressure than niobium metal at elevated temperature.

Because of this vapor pressure difference, purification is performed commercially by electron beam melting. This process can achieve very high superheat and liquid convection that rapidly boils off impurities. After several consecutive electron beam melting steps both aluminum and oxygen levels are reduced to less than 50ppm. Other naturally occurring impurities with low vapor pressure such as tantalum and tungsten can not be removed by electron beam melting. These impurities must be removed by other liquid extraction methods prior to aluminothermic reduction. Typical production electron beam furnaces are now 500 - 2000 KW of beam power (4) and are capable of purifying ingots 300-500 mm in diameter, and over two meters long. A two-gun 600KW 1970's vintage production furnace is shown in Figure 1. The design of these furnaces is usually specific to each manufacturer but a very high volume diffusion pumping system is always required to keep up with the high gas load during melting. Typically several 700-1200 mm diameter oil diffusion pumps are needed on each furnace to keep vacuum levels below 10^{-5} torr during melting. Electron guns are also independently pumped from the main chamber to achieve a higher vacuum level in the beam generation portion of the guns. This greatly increases the reliability of electron guns. In the future even larger furnaces will incorporate commercially available electron guns that can now emit over 1 MW in a single electron beam.



Figure 1: Typical electron beam melting furnace used for purifying niobium metal. Two 300KW electron guns on this furnace are capable of melting 300 mm diameter ingots.

Niobium alloys are made by subsequent vacuum arc remelting with the appropriate elemental additions. The most common alloy additions are zirconium, titanium, and hafnium as shown in Table I. Higher melting temperature elements such as tungsten or tantalum can be added by electron beam melting, or as a master

alloy in vacuum arc melting. Even though vacuum arc melting is commonly used for alloy steels, nickel and titanium alloys, it should be noted that the high melting temperature of niobium requires much higher power levels. It is not unusual to melt 200 mm diameter ingots using 15- 20,000 amperes of current. Some alloys such as Nb-1Zr are notorious for arcing against the crucibles and burning into the water jacket during melting. Intensive water cooling is required to minimize this risk.

Table I Commercially available niobium alloys for high temperature use

Alloy	Composition (wt%)	Density (gm/cm³)
C-103	Nb-10Hf-1Ti	8.85
Nb-1Zr	Nb-1Zr	8.57
PWC-11	Nb-1Zr-0.1C	8.57
WC-3009	Nb-30Hf-9W	10.1
FS-85	Nb-28Ta-10W-1Zr	10.6

Fabrication of Niobium Alloys

Niobium alloys are initially hot worked at or slightly above the alloy recrystallization temperature, which is typically 1000-1350°C for the various commercial alloys. Either forging or extrusion can be used. Extrusion or hammer forging are the preferred methods for smaller ingots, which tend to lose heat too rapidly for conventional press forging. Compared to other more common materials like steel or titanium alloys, niobium alloys have high flow stresses at hot working temperature. This can lead to very high pressures on metalworking equipment tooling. Items like extrusion dies are typically used only once and then must be replaced due to high erosion. During hot working all niobium alloys develop a layer of surface contamination from reaction with air. This layer is very brittle and must be removed by machining or grinding prior to any subsequent cold working. Secondary fabrication is performed by warm or cold working to final shapes with appropriate stops for recrystallization annealing, which is performed under high vacuum. Most commercial alloys are ductile enough to be processed into various mill products such as sheet, foil, rod, wire and tubing, often with cold reductions in excess of 70%.

Niobium alloy mill products can be fabricated into various complex shapes by almost all of the common metal forming processes, such as closed die forging, spinning, hydroforming, welding, etc. Examples of closed die forgings and a shear spun rocket nozzle are shown in Figures 2, 3. The relatively low density of niobium alloys, combined with their ease of fabrication, frequently favors niobium alloys as compared to other refractory metals such as molybdenum, tantalum or tungsten.

Pure unalloyed niobium is extremely ductile, even in the cast condition. Ingots can be cold worked extensively (in excess of 95%) without annealing. Improved grain size uniformity however, can be achieved with periodic recrystallization annealing after multiple cold working steps. Annealing temperature and the amount of cold working also have a combined effect on the resultant grain structure. The effect of these variables on hardness is shown in Figure 4 for high purity RRR grade niobium. The high purity level of this grade of niobium reduces the recrystallization temperature to approximately 700°C. Commercial purity niobium recrystallizes at ~900°C.

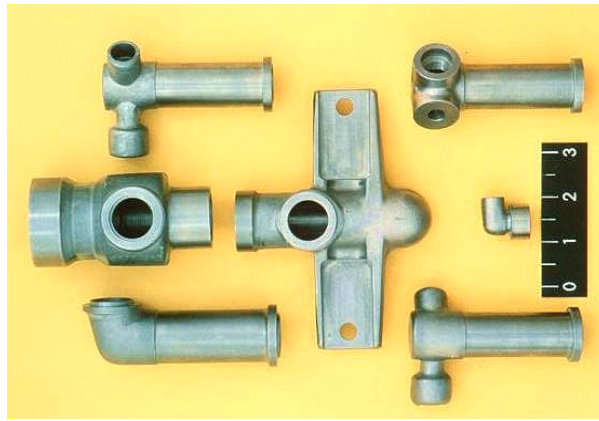


Figure 2: Closed die forgings fabricated from C-103 alloy.

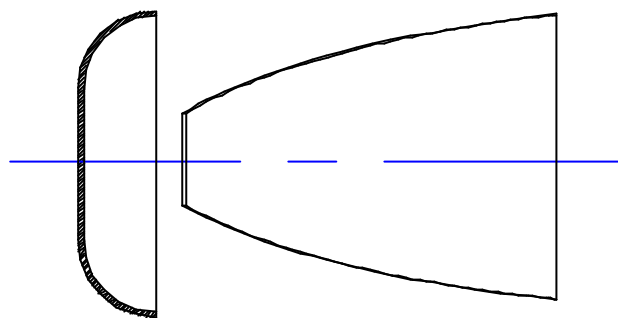


Figure 3: Rocket thrust cone fabricated from C-103 alloy showing pressed plate preform and shear spun final shape. Final diameter ~600mm x 1-2mm wall thickness.

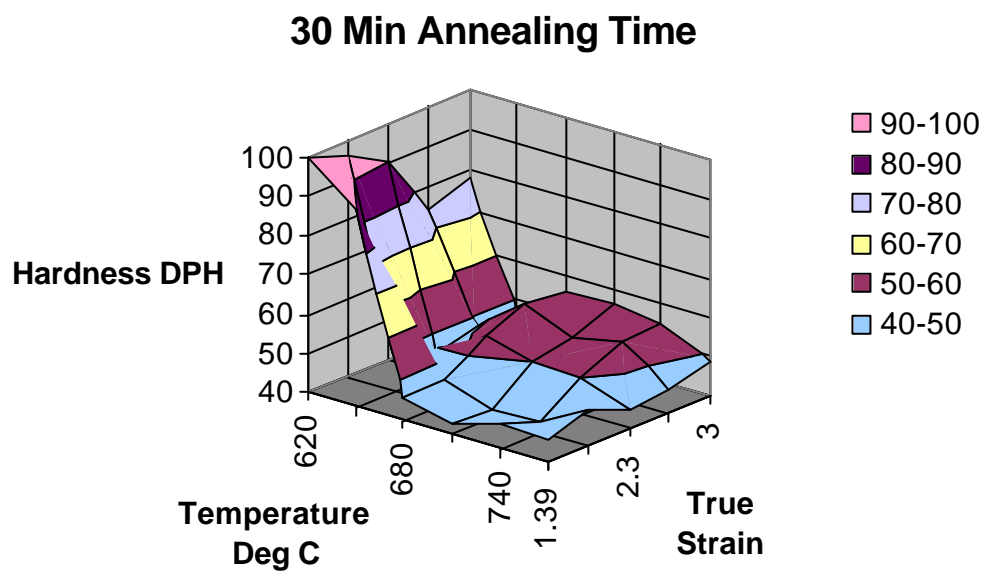


Figure 4: Effect of annealing temperature and cold working on final hardness of RRR grade niobium plate 1-3 mm thick.

Alternate Fabrication Methods for Niobium Alloys

During the early 1980's there were several programs aimed at producing niobium alloy parts by more cost-effective methods. Several attempts were made to manufacture niobium alloy net shape parts by investment casting. This method presented some special challenges to avoid extensive reaction with the shell mold, and to get enough superheat into the metal to avoid cold laps. While it was demonstrated that casting is possible even for niobium alloys with melting temperatures over 2400°C, the "as cast" microstructure is typically less ductile than normal wrought microstructures.

The economic aspects of producing niobium alloy castings was also severely hindered by the loss of metal in the form of gates, skull, and risers. Unlike titanium and nickel alloys, the gates and other casting scrap are not remeltable for niobium alloys due to the low tolerance for interstitial impurities. An investment cast C-103 alloy turbine engine stator is shown in Figure 5. At this time no niobium alloy parts are made by this method.

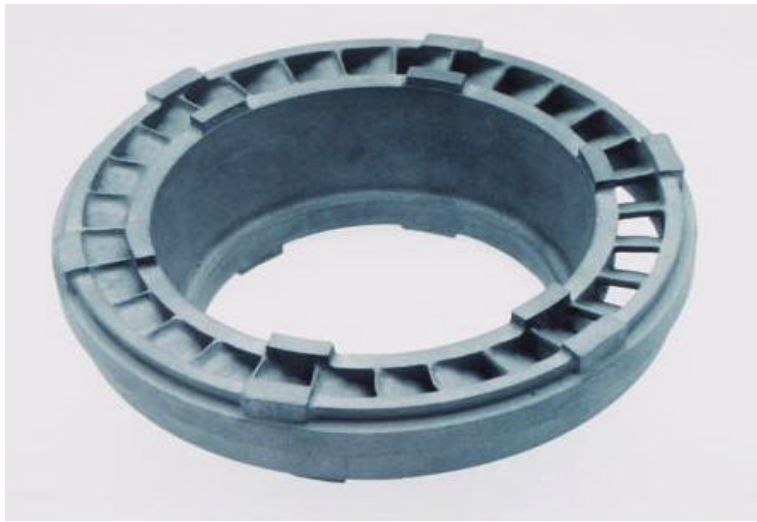


Figure 5: Investment cast C-103 stator ring produced by Precision Cast Parts.

Considerable research effort was also devoted to powder metallurgy process development. Two niobium alloys, C-103 and a high-strength alloy, WC-3009, were evaluated after preparation by a variety of powder metallurgy processes, including rapid solidification methods (5), hot isostatic pressing and vacuum sintering. The most difficult aspect of processing niobium alloys by powder methods is preparation of the alloys into powder. These difficulties arise from the high melting temperature and reactive properties of the alloys, which contain elements such as hafnium, titanium, and zirconium. High purity powder can be manufactured only by the hydride-dehydride process or atomization in a crucible free process. Centrifugal atomization has been successfully used for producing powder. Either an electron beam (EBA process) or plasma torch (PREP process) can be used as the heat source for centrifugal atomization. In summary, these programs demonstrated that niobium alloys can be made by powder metallurgy methods and the level of interstitial impurities can be kept low. It was however also determined that net shapes could not be produced economically due to the high production cost of centrifugally atomized powder (PREP and EBA processes). Consequently no niobium alloy parts are made by powder metallurgy at this time. Some of the developmental parts and properties of the powder processed niobium alloy are shown in Figure 6 and Table II.

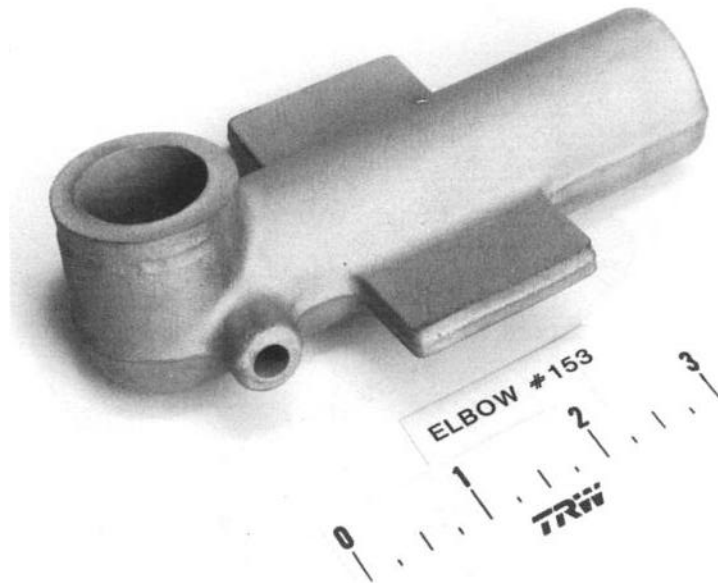


Figure 6: Net shape C-103 part produced by hot isostatic pressing spherical powder in steel can with ceramic cores.

Table II Tensile properties of powder processed C-103 alloy

Process method	0.2%Yield at 20 ⁰ C (Mpa)	0.2%Yield at 1200 ⁰ C (Mpa)
Wrought (normal process)	296	110
HIP PREP powder	285	121
HIP hydride/dehydride powder	282	120

Powder metallurgy processing was also explored for making porous niobium structures to withstand high heat flux as anticipated in the National Aerospace Plane (NASP). The ability to manufacture porous structures and the compatibility of niobium alloys with liquid lithium make it an ideal material for lithium cooled heat pipes. Additionally, the history of using protective silicide coating on niobium alloys for oxidation resistance in turbine afterburners and liquid fuel rockets made niobium alloys an ideal candidate material for a variety of other hypersonic structures. Both leading edges for wings, and nose cones were designed and successfully fabricated to function as heat pipe thermal management systems. Using the heat pipe principle, these structures were designed to transport extreme heat away from hot spots, such as hypersonic leading edges, to cooler areas where heat could be expelled by radiation. A C-103 alloy heat pipe in operation is shown in Figure 7. In this figure the heat pipe, that is silicide coated, is being heated at its midpoint by a standard oxygen/mapp gas-cutting torch. Under these test conditions a normal piece of silicide coated C-103 would reach 1800-1900°C in seconds and then begin burning. The heat pipe, however, resists overheating by absorbing the heat flux and then using this energy to convert liquid lithium into lithium vapor inside the sealed heat pipe. A typical 500-gram niobium heat pipe can dissipate over 10 kilowatts of heat and operate isothermally at 1250-1350°C. These devices were successfully tested in combustion torches, high velocity jet fuel burners (6), tungsten quartz lamps, and even electric welding arcs at heat fluxes well over 1000 watts/cm² (7). Unfortunately, this successful work was suspended when the NASP program ended.

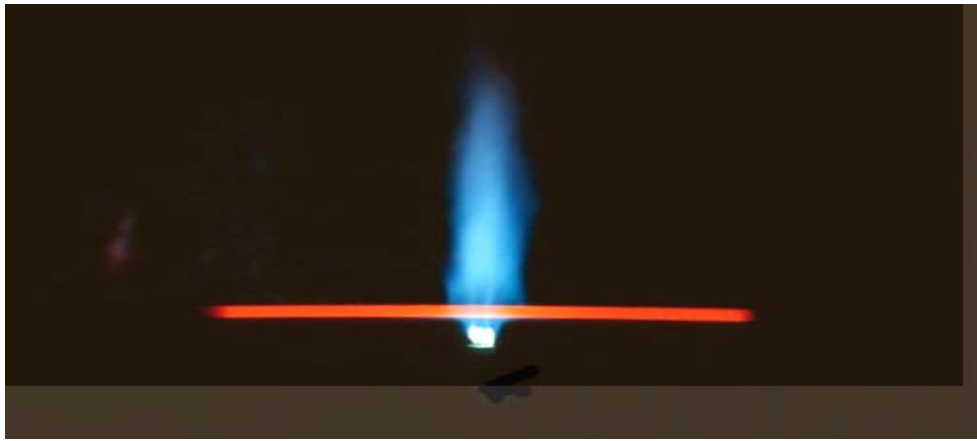


Figure 7: Niobium alloy heat pipe that was used in a leading edge designed to resist hypersonic aerothermal heating.

Properties of Commercial Alloys

The most common high-temperature niobium alloys are listed in Table I. All these alloys are hardened primarily by solid solution strengthening, however, small amounts of second-phase particles are present. The composition of these particles varies, but they are generally associated with interstitial impurities that form oxides, nitrides, and carbides. Often the size and distribution of second phases can have a strong influence on mechanical properties and recrystallization behavior (8). A variation of the Nb-1Zr alloy, commonly known as PWC-11, contains an intentional addition of 0.1 weight percent carbon specifically to form carbide precipitates, which significantly improve high-temperature creep properties.

One of the other alloys listed, WC-3009, contains ~0.10 weight percent oxygen, which is approximately five times more oxygen than other niobium alloys. This high level of oxygen is introduced as a result of powder processing. It is not deleterious to mechanical properties because the oxygen combines with hafnium in the alloy to form stable hafnium oxide precipitates. The WC-3009 alloy is unique in that it exhibits an oxidation rate less than one tenth that of most other niobium alloys (3). When WC-3009 was developed, it was speculated that such an alloy could survive a short supersonic mission even in the event of a protective coating failure.

Alloys that contain second-phase particles, which have formed a continuous boundary between grains, can exhibit drastically reduced tensile elongation (5). This undesirable condition is usually caused by contamination or improper heat treatment. In general, niobium alloys are much less tolerant of impurity pickup than other reactive metals such as titanium and zirconium alloys. Copper, which can accidentally be introduced in welding operations, is particularly disastrous to mechanical properties. The total interstitial oxygen, hydrogen, carbon, and nitrogen content of niobium alloys are typically one-fifth to one-tenth that of titanium or zirconium alloys.

Tensile properties of the common alloys at 20°C are given in Table III. All the commercial alloys are very ductile at room temperature. The highest tensile strength at room temperature and elevated temperature, Figure 8, is exhibited by WC-3009 alloy. Creep stresses for 1% strain in 100 and 1000 hours are summarized in Figures 9 and 10. Even though WC-3009 clearly exhibits the highest tensile strength, FS-85 has superior creep strength, due to its higher melting point from the alloy's high concentration of tantalum and tungsten.

Table III Typical Room Temperature Tensile Properties of Niobium Alloys

Alloy	Yield strength, (MPa)	Ultimate, (MPa)	Elongation,%
C-103	296	420	26
Nb-1Zr	150	275	40
PWC-11	175	320	26
WC-3009	752	862	24
FS-85	462	570	23

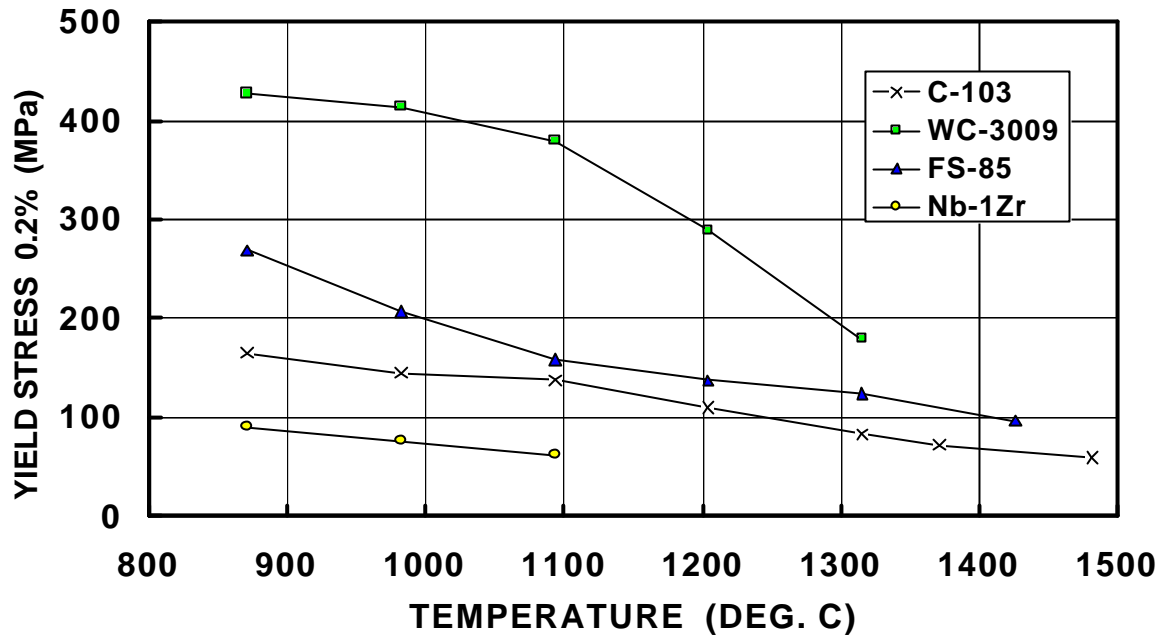


Figure 8: Tensile yield strength vs. temperature for common niobium alloys.

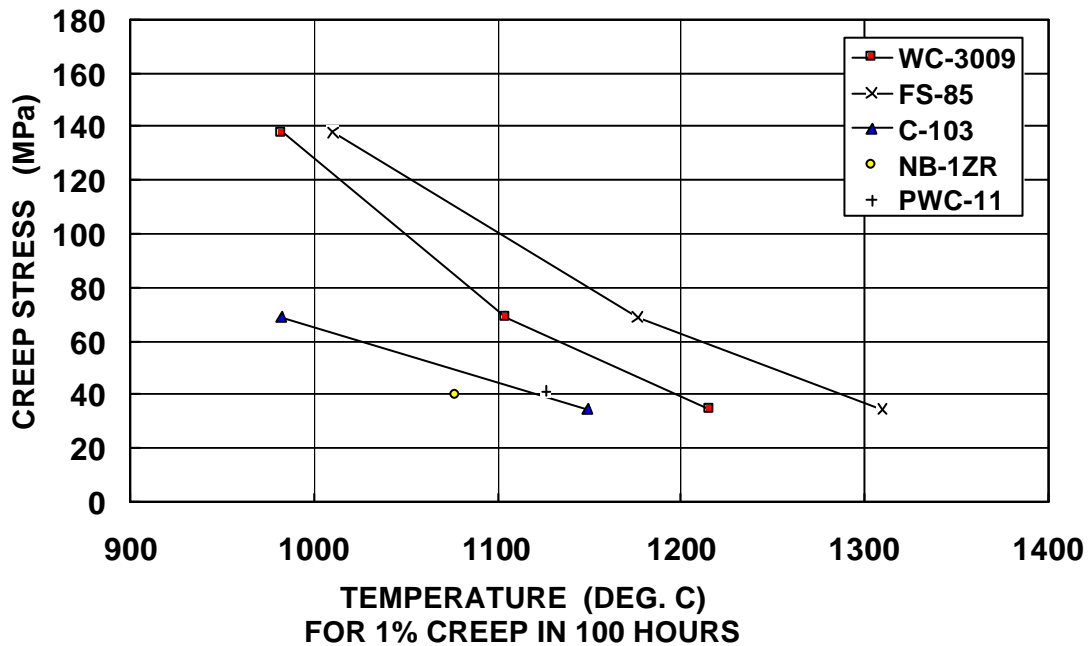


Figure 9: Stress to produce 1% creep after 100 hours (5, 9-11).

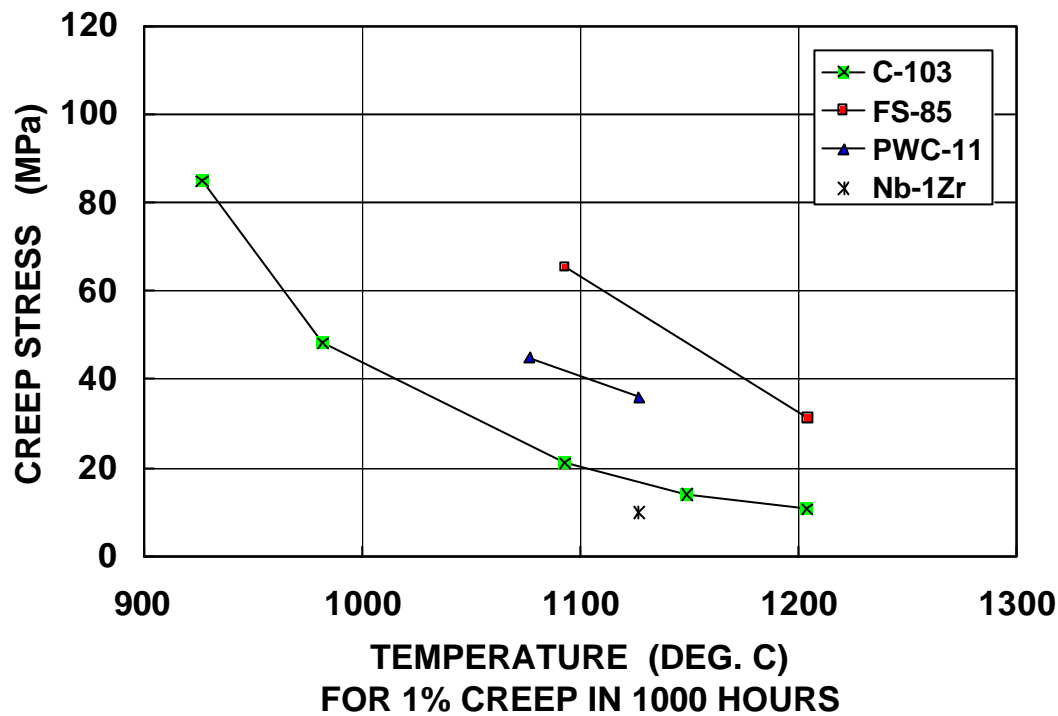


Figure 10: Stress to produce 1% creep after 1000 hours (5,9-11).

Elastic modulus, thermal conductivity, and total hemispherical emissivity are listed in Tables IV - VI. The emissivity data are for smooth and non-oxidized surfaces that exhibit much lower emissivity values than oxidized material. Also shown in Table 6 is an emissivity value of 0.7-0.82 for silicide coated C-103. This value is for a common Si-20%Fe-20%Cr coating applied by the slurry coat and fusion method. Thermal expansion data are shown in Figure 11.

Table IV Elastic Modulus for Common Niobium Alloys

ALLOY	ELASTIC MODULUS, (GPa)	
	20°C	1200°C
C-103	90	64
Nb-1Zr	80	28
WC-3009	123	
FS-85	140	110

Table V Thermal Conductivity of Niobium Alloys

ALLOY	800°C, (W/m°C)	1200°C, (W/m°C)
C-103	37.4	42.4
FS - 85	52.8	56.7
Nb - 1Zr	59.0	63.1

Table VI Total Hemispherical Emissivity for Common Niobium Alloys

ALLOY	TOTAL EMISSIVITY	
	800°C	1200°C
C - 103	0.28	0.40
Nb - 1Zr	0.14	0.18
C - 103 (silicide coated)	0.70 - 0.82	

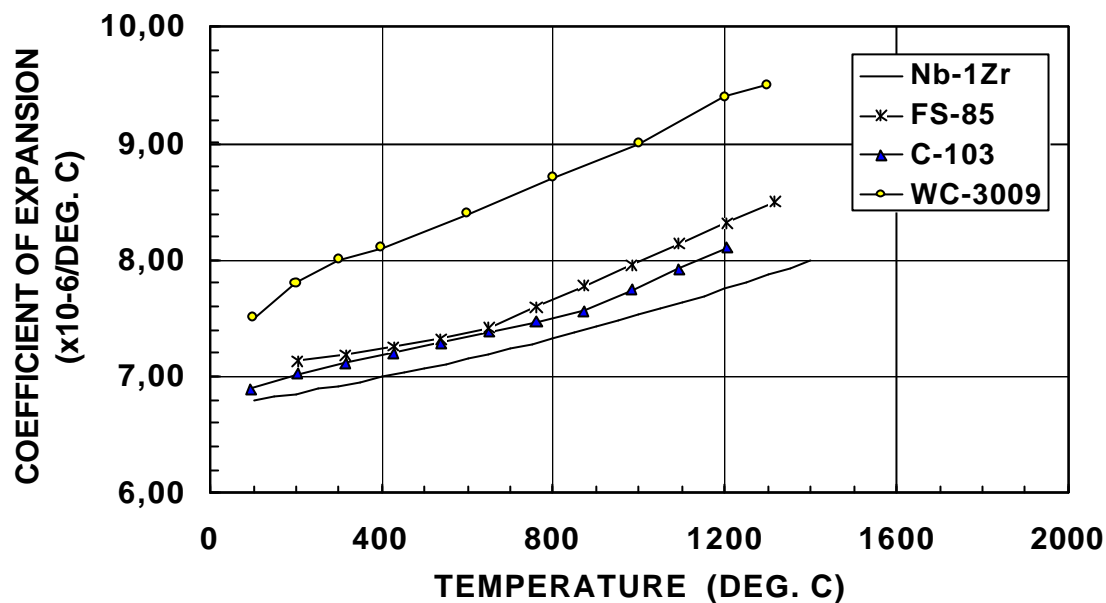


Figure 11: Thermal expansion coefficient for various niobium alloys at elevated temperatures.

Conclusion

In summary, we have briefly described the processing and thermomechanical properties of commercial high-temperature niobium alloys. Other improved alloys, composites, and new intermetallic materials are increasingly challenging applications for these alloys. Frequently, however, users are finding that these newer materials cannot be easily or economically fabricated into the desired shapes required. In other instances, users of high-temperature materials are rediscovering that advanced nonmetallic and composite materials may be more limited by their low thermal conductivity than metal alloy systems. As designers continue to develop experience with other less ductile high - temperature materials, it is most likely that the higher strength and less fabricable niobium alloys will also be reevaluated, especially if improved protective coatings are developed.

References

- (1) R.G. Frank, "Recent Advances in Columbium Alloys," Refractory Metal Alloys, (Plenum Press, 1968), 325 - 365.
- (2) J.A. Cornie, "Development of Precipitation Strengthened Columbium Base Alloys," (AFML-TR-71-5, December, 1971).
- (3) T.K. Roche and D.L. Graham, "Development of Oxidation Resistant, High Strength, Columbium Alloys," (AFML-TR-69-344, January, 1970).
- (4) R. Bakish, "Electron Beam Melting and Refining State of the Art 1985," Conference Proceedings, (Library of Congress, ISSN 0740 - 8706, November 1985).
- (5) C. C. Wojcik, "Evaluation of Powder Metallurgy Processed Nb-30HF-9W," MPIF, 1988

- (6) C. Wojcik and K. Jordan, Unpublished research ,1992.
- (7) C. Wojcik and L. Clark, "Design, Analysis, and Testing of Refractory Metal Heat Pipes Using Lithium as the Working Fluid," AIAA Thermophysics Conference, June 1991.
- (8) R.M. Bonesteel, D.J. Rowcliffe and T.E. Tietz, "Mechanical Properties and Structure of Internally Oxidized Niobium-1% Zirconium Alloy," TransTIM, Vol. 9 Supplement (1968).
- (9) R. Titran and W. Klopp, "Long Time Creep Behavior of the Niobium Alloy C-103," NASA TP-1727, (1980).
- (10) R. Titran and R. Hall, "High Temperature Creep Behavior of a Columbium Alloy, FS-85," NASA TN – D -2885, 1965.
- (11) R. Titran, "Long-Time Creep Behavior of Nb-1Zr Alloy Containing Carbon," NASA TM, 1986.