NIOBIUM AND NIOBIUM 1% ZIRCONIUM FOR HIGH PRESSURE SODIUM (HPS) DISCHARGE LAMPS

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Abstract

Niobium offers a unique combination of properties for use in High Pressure Sodium (HPS) vapor lamps. Today, both pure niobium and Nb-1Zr find use as lead wires and end caps in HPS lamps. The results of a statistical comparison of the mechanical properties of niobium and Nb-1Zr sheet and wire are presented, and reveal that the addition of 1% zirconium does not significantly alter the room temperature strength of niobium. Instead, the alloy exhibits enhanced mechanical properties at elevated temperatures compared to pure niobium. This observation, as well as metallurgical analysis, confirms that zirconium acts as a dispersion strengthener in niobium.

Introduction

The "Eureka", or first glow of a sodium vapor lamp occurred at Westinghouse's Newark facility over thirty years ago. In the initial lamp designs, the critical metal parts in contact with the quartz arc tube containing the sodium vapor were constructed of tantalum. For production, niobium parts quickly replaced tantalum end-caps and lead wires; niobium offered similar resistance against corrosive attack from high-pressure sodium as tantalum at a 75% cost saving. Today, niobium-1% zirconium (Nb-1Zr) is the prominent material of choice for the critical metal parts in High-Pressure Sodium (HPS) discharge lamps.

The selection of niobium and Nb-1Zr for use as the critical metal parts in HPS lamps is justified by several factors:

- The metal and the alloy exhibit excellent resistance to high-pressure gases contained in the arc tube (sodium, mercury, and xenon) at lamp operating temperatures [1].
- The coefficients of thermal expansion (CTE) of niobium and Nb-1Zr are similar to the polycrystalline alumina (Lucalox), as well as to the more recently developed ceramics used to construct the arc tube. This assures the integrity of the seal between the arc tube and its end-caps through thermal cycling during the lamp's service life.
- The thermal conductivity of niobium and Nb-1Zr is about triple that of there next-best alternative, nickel-base alloys. The materials' conductivity, combined with their high melting points, assures that there are no incipient melting issues.
- Niobium and Nb-1Zr are malleable and can be readily formed into desired shapes under ambient conditions.

Optimizing the service life of HPS discharge lamps is of dire importance to the light manufacturer who must reimburse municipalities for the replacement costs (including equipment and labor) of streetlights that fail prematurely. The life of HPS lamps can average as much as 24,000 hours, or the equivalent of over 6½ years assuming 10 light hours per activation [1]. The life of the HPS lamps is not limited by failure of the critical metal parts, but from the build-up of deposits that raise the operating voltage. When the ballast can no longer supply the increased voltage needed to sustain the arc, the lamp will flicker on and off and must be replaced.
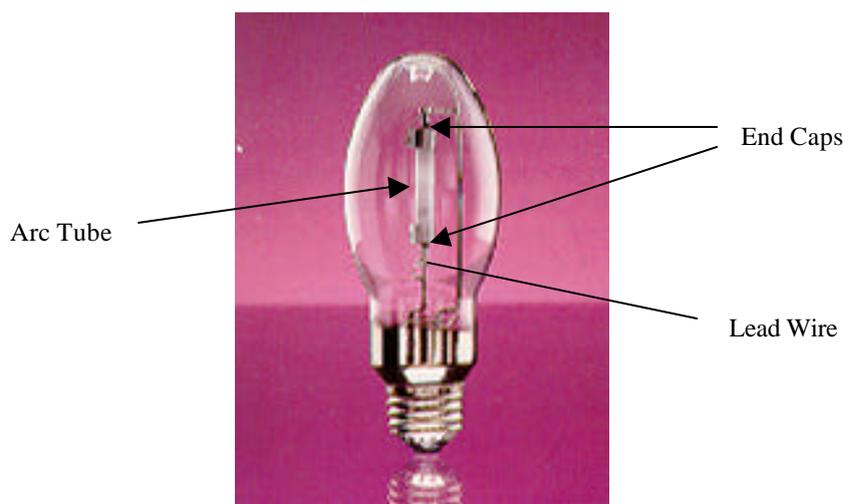
Figure 1: High Pressure Sodium (HPS) discharge lamp showing the arc tube and critical metal parts. Photograph courtesy of ALMIS [2].

Processing of Niobium and Nb-1Zr for Lighting Applications

High purity niobium and Nb-1Zr ingots are melted at Cabot Performance Materials' Boyertown Plant. Niobium billets, produced from Nb_2O_5 by the aluminum thermite process, are triple electron beam (3EB) melted in a 1200KW Leybold furnace to yield a high purity niobium ingot. Alloying niobium with zirconium is accomplished by Vacuum Arc Remelting (VAR). Here, VAR melting is used to minimize volatilization of the zirconium that would occur during EB melting. A comparison of the ingot chemistries of niobium and Nb-1Zr is given below.

Table I ASTM chemistry limits for niobium and Nb-1Zr [3]

	Zr	Ta	Fe	Si	W	Ni	Mo	Hf	Al
Niobium	0.02	0.2	0.01	0.005	0.05	0.005	0.01	0.02	0.005
Nb-1Zr	0.08-1.2	0.5	0.01	0.005	0.05	0.005	0.05	0.02	0.005

	O	C	N	H
Niobium	400	150	100	15
Nb-1Zr	400	150	100	15

Cabot controls the zirconium content to ±0.20% in Nb-1Zr products. The alloy's malleability is similar to that of pure niobium, and is processed in a similar manner into wire and strip. The finished wire used for HPS lamp applications typically ranges from 0.015 to 0.040 inch diameter, and sheet thickness runs from about 0.010 to 0.025" gauge.

Effect of Zirconium on the Properties of Niobium

While both niobium and Nb-1Zr find use in HPS lamps, the alloy serves to improve the mechanical properties of niobium at elevated temperatures. First, as evident in Figure 2, Nb-1Zr retains its strength up to temperatures of about 750ºC, whereas niobium quickly loses mechanical strength beyond about 500ºC. Similarly, the alloy remains rigid up to a temperature of about 750ºC, while the pure metal rapidly become soft and extremely ductile at higher temperatures above 500ºC. This behavior is seen in the tensile ductility plots given in Figure 3.

The addition of 1% zirconium also serves as a grain refiner for niobium. The grain size of the fine wire and strip products average about 10-20 microns, regardless of composition, due to the extensive amount of work imparted in the products from the deformation processes. However, the rate of grain growth of the pure metal is greater than that of the alloy. As a result, in high temperature service applications, Nb-1Zr is expected to be less prone to embrittlement than pure niobium.

The means by which zirconium stabilizes the elevated temperature properties of niobium has not been extensively investigated. The prevailing theory is that zirconium forms a second-phase by reacting with free interstitial oxygen atoms within the niobium matrix. As seen in Figure 4, a zirconium rich phase is present in niobium as large dispersoids within a cross section of annealed Nb-1Zr wire. These second-phase particles act as dispersion strengtheners, and are believed to be responsible for the high temperature properties and resistance to grain growth associated with the alloy compared to pure niobium.
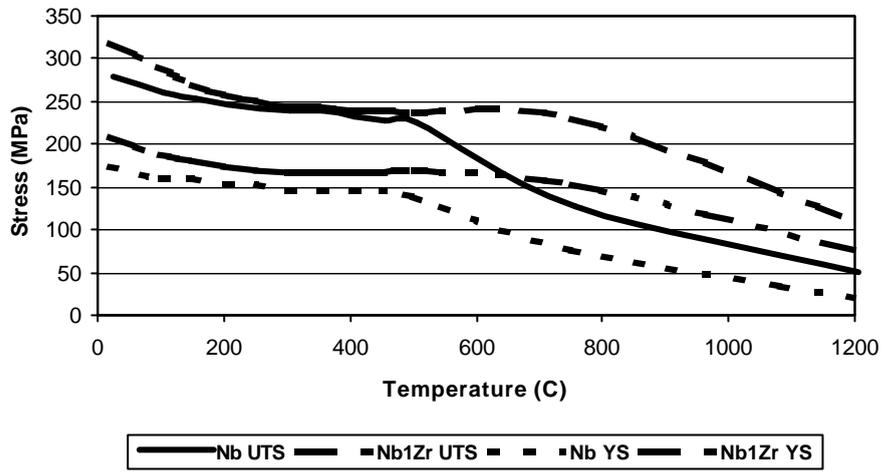
Figure 2: Effect of temperature on the Yield Strength (YS) and Ultimate Tensile Strength (UTS) of niobium and Nb-1Zr[4.5].
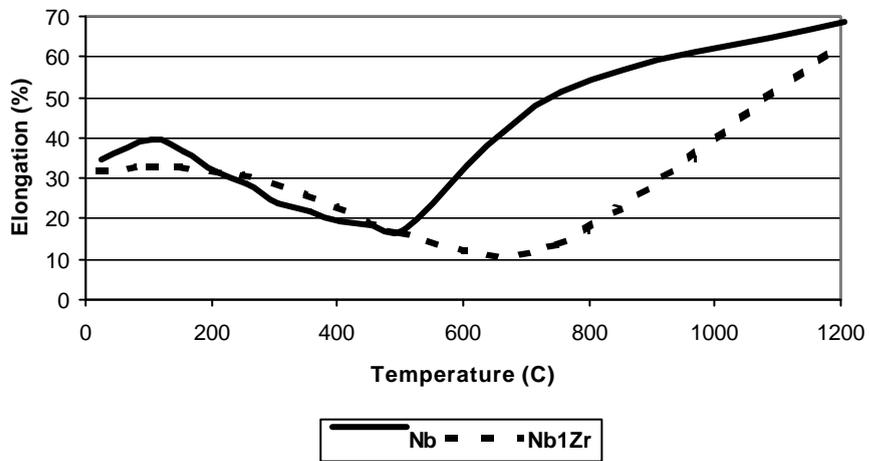
Figure 3: Effect of temperature on the ductility of niobium and Nb-1Zr[4,5].
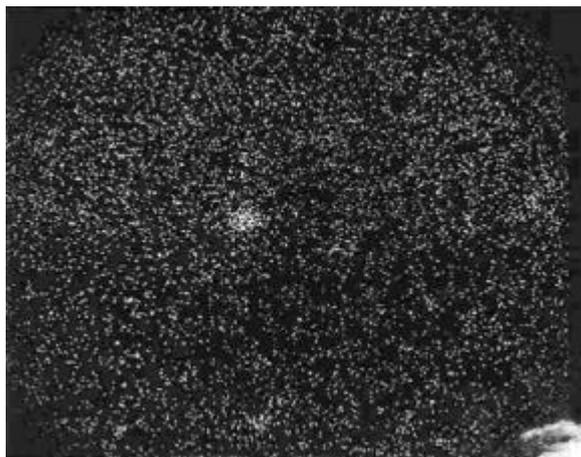
Figure 4: Dispersion of zirconium-rich phase through out the cross section of a Nb-1Zr wire.

To gain additional insight into the influence of zirconium on niobium, the mechanical properties of niobium and Nb-1Zr wire and sheet were collected from historic production records and analyzed using statistical methods.   The ambient temperature mechanical properties were collected from 242 lots of niobium wire and from 238 lots Nb-1Zr wire. In addition, data representing 146 lots of niobium strip and 503 lots of Nb-1Zr strip was also compared.

The results from the statistical evaluation of tensile strength and elongation data from the wire and strip products are reported numerically in Tables II and III, respectively. The statistical data is also presented graphically as box plots, where the second and third quartiles are represented as boxes and the first and fourth quartiles are indicated by lines. The box plots comparing the Ultimate Tensile Strength (UTS) and elongation of niobium and Nb-1Zr wire are given in Figure 5, while those comparing the properties of niobium and Nb-1Zr strip are provided as Figure 6.

Table II Statistical comparison of niobium and Nb-1Zr wire room temperature mechanical data

Composition	Median	Mean	Std. Deviation	Range
Ultimate Tensile Strength (ksi)				
Niobium	42.1	42.3	3.1	34.5-50.9
Nb-1Zr	42.8	43.0	2.4	34.9-48.4
Elongation (%)				
Niobium	31.4	31.2	3.7	21.2-40.0
Nb-1Zr	27.2	27.4	2.5	20.1-32.5

Table III Statistical Comparison of niobium and Nb-1Zr sheet room temperature mechanical data

Composition	Median	Mean	Std. Deviation	Range
Ultimate Tensile Strength (ksi)				
Niobium	45.6	46.3	4.8	38.5-55.2
Nb-1Zr	42.8	43.0	2.4	34.9-48.4
Elongation (%)				
Niobium	25.4	26.0	4.4	17.6-39.2
Nb-1Zr	27.2	27.4	2.5	20.1-34.5
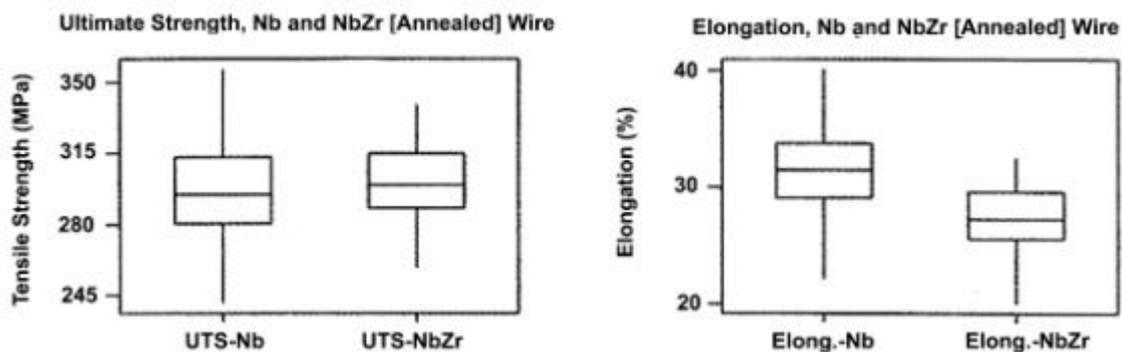
Figure 5: Box-plots comparing the distribution of tensile strength values (left) and elongation values (right) for annealed niobium and Nb-1Zr wire.
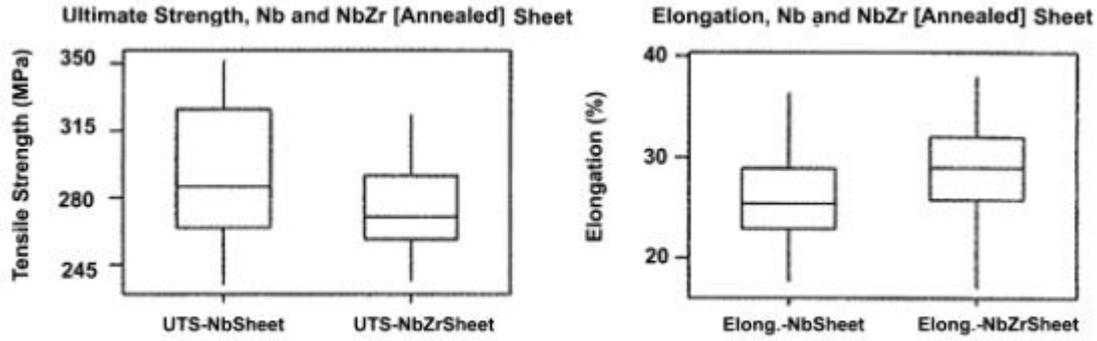
Figure 6: Box-plots comparing the distribution of tensile strength values (left) and elongation values (right) for annealed niobium and Nb-1Zr wire.

Surprisingly, the statistical results reveals that the addition of 1% zirconium does not alter the ambient temperature ultimate tensile strength (UTS) of niobium wire. Comparative evaluation using *t-distribution* analysis demonstrated that there is no statistically significant difference in means between the UTS of niobium and Nb-1Zr wire within a 0.95 confidence limit (P-value = 0.0080). Subsequent analysis on historic tensile strength data of thin gauge niobium and Nb-1Zr strip also support this finding.

Discussion of Results

The observation that zirconium additions have a more prevalent effect on the mechanical properties of niobium at elevated temperatures as opposed to ambient temperatures is founded in crystal mechanics. The flow stress (s) is comprised of two components:

$$\boldsymbol{s} = \boldsymbol{s}_t + \boldsymbol{s}_a \tag{1}$$

where s_t = thermal stress component;
s_a = athermal stress component.

The thermal stress component accounts for the contribution of thermal energy to overcoming the short-range barriers to dislocation motion. For body centered cubic (BCC) metals including niobium, temperature-sensitive barriers include the Peierls stress and Cottrell atmospheres formed by mobile interstitials[6]. Conversely, the athermal stress component represents the impact of long-range barriers to slip, such as expected from second-phase, zirconium-rich dispersoids within the matrix. At room temperature, the tensile strength of niobium may be influenced predominantly by the effect from interstitials than by the addition of 1% zirconium. However, at elevated temperatures where the contribution of the thermal stress component becomes insignificant, the effect of zirconium on increasing the athermal stress component of niobium becomes apparent.

If zirconium serves as a solid solution strengthener in niobium, a statistically significant difference in the room temperature tensile strength of the metal and alloy would have been evident. In this scenario, the short-range stress fields in the matrix created by the substitutional zirconium atoms would impeded dislocation motion and increase the work hardening rate. This would have acted to increase the ambient temperature ultimate tensile strength of the alloy.

The difference in elongation properties of niobium and Nb-1Zr wire may be due more to physical differences of the geometry of the test specimens than from the mechanical properties of the materials. Elongation is an extrinsic material property; and factors such as sample dimensions directly effect measured elongation to failure values. Specifically, the shorter the gauge length, or the greater the cross sectional area of the sample, the greater the contribution of the localized necking region to the measured elongation[7].

$$e_f = b \frac{\sqrt{A_0}}{L_0} + e_u \qquad (2)$$

Where e_f = elongation at failure;
A_0 = cross section of tensile test sample;
L_0 = gauge length of tensile test sample;
e_u = strain at ultimate stress.

Although the gauge length of the niobium and Nb-1Zr wire samples was constant, the average diameter differed between materials. The niobium wire diameter ranged from 0.25-0.040 inches, compared with Nb-1Zr wire which ranged from 0.15-0.30 inches in diameter. Thus, the measured ductility of the Nb wire would be expected to be greater than that measured for Nb-1Zr wire, as seen in Figure 5. This hypothesis is confirmed by comparing the measured ductility of niobium and Nb-1Zr sheet shown in Figure 6. The average ductility of 0.010-0.015 inch gauge niobium sheet is measured to be lower than that measured from the heavier 0.010-.025 inch gauge Nb-1Zr sheet.

Summary

Niobium and Nb-1Zr are the materials of choice for High Pressure Sodium (HPS) Discharge lamps since the material characteristics match service requirements.

- The metal and the alloy exhibit high melting points. There are no incipient melting issues.
- The coefficient of thermal expansion (CTE) is similar to quartz and other ceramics employed to contain the sodium vapor. The CTE of niobium and Nb-1Zr is about half that of nickel-base alloys.
- The thermal conductivity of niobium and Nb-1Zr is about triple that of nickel-base alloys.
- The metal and the alloy exhibit excellent resistance to sodium vapor at lamp operating temperatures.
- Niobium and Nb-1Zr mill forms are easily fabricated and assembled into lamp parts at room temperature.

The addition of 1% zirconium does not have a statistically significant effect on the room temperature strength of niobium wire or sheet. However, Nb-1Zr offers improved high temperature properties compared to commercially pure niobium. These observation supports findings that zirconium acts as a dispersion strengthener in niobium. Additional information pertaining to the test sample geometry is required in order to quantify the effect of zirconium on the ductility of niobium.

Acknowledgements

References

(1) "High Pressure Sodium Lamps", *Pacific Energy Fact Sheet*, Pacific Gas and Electric Company (May, 1997), pp.1.

(2) "High Pressure Sodium Lamps", ALMIS Light Sources, http://www.arch.uiuc.edu/courses/arch242/arch242/sources/hid_sod/htm

(3) "Standard Specification for Niobium and Niobium Alloy Bar, Rod, and Wire", ASTM B 392-95, American Society of Testing of Materials, West Conshohocken, PA.

(4) "Niobium Metallurgical Products", Cabot Corporation, 1996.

(5) http://www.tantalum central.com.

(6) C.A. Michaluk, G.T. Gray III, and T. Chatterjee, P/M in Aerospace, Defense and Demanding Applications, Metal Powder Industries Federation, Princeton, (1993), pp. 195.

(7) M.J. Barba, *Mem. Soc. Ing. Civils*, Part 1, (1880), pp. 682.