VARIATION OF MECHANICAL PROPERTIES OF HIGH RRR AND REACTOR GRADE NIOBIUM WITH HEAT TREATMENTS

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VARIATION DES PROPRIÉTÉS MÉCANIQUES DU NIOBIUM DE HAUT RRR ET DE QUALITÉ "Réacteur" SELON LES TRAITEMENTS THERMIQUES

RÉSUMÉ: Les cavités rf supraconductrices utilisées pour l'accélération des particules sont faites en niobium de haute pureté, de rapport de résistance résiduelle supérieur à 250. Le niobium de qualité "réacteur" est aussi utilisé pour la fabrication de guides d'onde et/ou de composants terminaux des structures accélératrices. Les impuretés majeures dans cette catégorie de niobium sont les éléments interstitiels en solution: hydrogène, azote, oxygène et carbone. Après fabrication, les structures accélératrices sont soumises à des traitements thermiques de plusieurs heures sous vide jusqu'à des températures de 900°C pour le dégazage de l'hydrogène ou de 1400°C pour améliorer notablement la conductibilité thermique du niobium. Ces traitements thermiques affectent énormément les propriétés mécaniques du niobium. Dans cet article sont présentées les variations de propriétés mécaniques du niobium de haute pureté et du niobium de qualité "réacteur", en fonctions des traitements thermiques dans un vide de $\sim 10^{-6}$ Torr, aux températures de 600°C à 1250°C, pendant des durées de 10 à 6 heures. Pour le niobium de haute pureté, le phénomène de limite d'élasticité supérieure et inférieure commence à apparaître, alors qu'il disparaît pour le niobium de qualité "réacteur", après traitement thermique à 1250°C en présence de Ti utilisé comme getter.

ABSTRACT. Superconducting rf cavities used as accelerating structures in particle accelerators are made from high purity niobium with residual resistance ratios greater than 250. Reactor grade niobium is also used to make wave-guide and/or end group components for these accelerating structures. The major impurities in this type of niobium are interstitially dissolved gases such as hydrogen, nitrogen, and oxygen in addition to carbon. After fabricating the niobium accelerating structures, they are subjected to heat treatments for several hours in vacuum at temperatures of up to 900°C for degassing hydrogen or up to 1400°C for improving the thermal conductivity of niobium considerably. These heat treatments are affecting the mechanical properties of niobium drastically. In this paper the variation of the mechanical properties of high purity and reactor grade niobium with heat treatments in a vacuum of $\sim 10^{-6}$ Torr and temperatures from 600°C to 1250°C for periods of 10 to 6 hours are presented. High purity niobium starts exhibiting upper and lower yield stress points while reactor grade niobium, on the other hand, stops exhibiting this characteristic BCC material behavior of upper and lower yield stress points after heat treatment at 1250°C in the presence of Ti as a solid state getter material.

Superconducting rf cavities used as accelerating structures in particle accelerators are made from high purity niobium with Residual Resistivity Ratio (RRR) values of greater than 250, corresponding to a thermal conductivity of approximately 60 W/m K at 4.2 K [1]. The major impurities in this type of niobium are interstitially dissolved gases such as hydrogen, nitrogen, and oxygen in addition to carbon.

The concentration of hydrogen tends to be somewhat higher near surfaces, interfaces, and other crystal defects, such as dislocations. At room temperature and hydrogen concentration < 6 atomic % there exists the BCC α -phase, while at higher concentrations or lower temperatures, ordered phases form. Notably the ϵ -phase forms below 200K, which can distort the niobium lattice so much that the superconducting critical temperature is reduced to $T < 1.3$ K [2]. In superconducting cavities the precipitation

of the ϵ -phase has been connected with " Q -disease" and it is reflected in a significant degradation of the Q -value (increased electrical losses by a factor of up to 100 have been observed.)

Q -degradation can be avoided by cooling a cavity quickly through the dangerous temperature region of $75\text{ K} < T < 150\text{ K}$ thus eliminating the precipitation of the ϵ -phase. However, this is not a permanent "fix"; the only known permanent cure is degassing of the hydrogen from the niobium to low ppm levels. In order to degas the niobium cavities, they are heated in vacuum at a temperature above 500°C ; at 800°C , for example, the hydrogen is degassed readily. However, it was recently observed with Spallation Neutron Source project (SNS) cavities, that a heat treatment at 800°C for even 1 hour degraded the mechanical properties of the material, in particular, decreasing the yield strength. In order to understand this reduced yield strength of high RRR niobium and also as a QC measure each vendor-supplied production niobium sample's mechanical properties were measured after heat treatments. In this paper the mechanical properties of both high purity and reactor grade niobium as a function of heat treatment temperature (600°C to 1250°C) are presented.

Experimental procedure

An Applied Test Systems tensile machine model ATS 900 was used for evaluating the niobium samples. The details of the sample preparation and mechanical properties measurement procedure were described elsewhere [1]. Two different strain rates namely slow strain rate (SSR) and fast strain rate (FSR) were used for making these measurements. The nominal SSR is $5.56 \times 10^{-5}\text{ s}^{-1}$ while FSR is $2.0 \times 10^{-4}\text{ s}^{-1}$ up to yield point and $1.0 \times 10^{-3}\text{ s}^{-1}$ until break. The accuracy of the strain measurement is $\pm 2\%$, while the accuracy of the stress and percentage of elongation is $\pm 1\%$.

Results and discussions

High RRR niobium

The Stress-Strain curves of the high RRR niobium are presented in Figures 1 to 4 for as received (ASR), heat treated at 600°C for 10 hours, heat treated at 800°C for 6 hours and heat treated at 1250°C in the presence of Ti solid state getter for 6 hours respectively. Table I summarizes the mechanical properties of high purity niobium. Vickers hardness (H_v) and the

RRR (an indication of the purity of the material) values are also included in the table.

The sharp increase in stress after a strain of larger than 0.007 in the stress-strain curves for some of the samples is due to the increment of strain rate from $2.0 \times 10^{-4}\text{ s}^{-1}$ to $1.0 \times 10^{-3}\text{ s}^{-1}$

Fig. 2 - Stress-strain curves of high RRR niobium heat treated at 600°C for 10 hours.

Fig. 2 - Courbes contrainte-déformation du niobium de RRR élevé, après traitement de 10 h à 600°C .

Fig. 3 - Stress-strain curves of high RRR niobium heat treated at 800°C for 6 hours.

Fig. 3 - Courbes contrainte-déformation du niobium de RRR élevé, après traitement de 6 h à 800°C .

Fig. 1 - Stress-strain curves of as received niobium.

Fig. 1 - Courbes contrainte-déformation du niobium dans l'état de réception.

Fig. 4 - Stress-strain curves of high RRR niobium heat treated at 1250°C for 6 hours with Ti.

Fig. 4 - Courbes contrainte-déformation du niobium de RRR élevé, après traitement de 6 h à 1250°C , en présence de Ti.

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until break. As can be expected, both the yield (0.2% offset) and tensile strength of the samples decreased with the heat treatments. Samples that were heat treated at 1250°C with Ti getter have shown high and low yield stress points. Such a characteristic is common in bcc metal behavior containing ppm concentrations of interstitial solid solutions [3]. However the impurity analysis presented in Table II does not show any increase in the interstitial content due to the heat treatment at 1250°C with Ti getter material. Perhaps the sensitivity of the analytical techniques may have to be improved. On the other hand internal friction measurements on these samples may provide the insight since this technique has atomic ppm level sensitivity for interstitials. In future, the interstitial content measurement will be made with the internal friction method.

A1, A2: vacuum annealed at 1250°C with Ti;
B1, B2: vacuum annealed at 800°C;
C1, C2: vacuum annealed at 600°C;
D1, D2: As received.

Method of analysis:

- O, N, H: Inert gas fusion in impulse furnace
O (Oxygen): NDIR (Non Dispersive Infra Red Absorption)
N (Nitrogen): TCD (Thermal Conductivity Detection)
H (Hydrogen): TCD (Thermal Conductivity Detection)
- C: Infrared light absorption during combustion in oxygen flow (high-frequency furnace method)
- Metal Impurities: Inductively Coupled Plasma - Atomic Emission Spectrometer

Reactor grade niobium

Figure 5 gives the stress-strain curves of reactor grade niobium as received (RGACCELASR), heat treated at 1100°C for 3 hours (RG11003Ti), 1200°C for 6 hours (RG1200Ti6) and at 1250°C for 6 hours (RG12506Ti) with Ti getter material. The strain rate used for these measurements is $5.56 \times 10^{-5} \text{ s}^{-1}$. Table III gives the summary of the mechanical properties of the reactor grade niobium as received and with various heat treatments. The RRR of the niobium is also presented in the table. As received material exhibited the well-known occurrence of

Fig. 5 - Stress-strain curves of reactor grade niobium with various heat treatments.

Fig.5 - Courbes contrainte-déformation du niobium de qualité "réacteur", après différents traitements thermiques.

Table I - Summary of the high RRR niobium mechanical properties.

Tableau I - Propriétés mécaniques du niobium de RRR élevé.

Niobium	Yield Strength (MPa)		Tensile Strength (MPa)		Elongation %		H_v	RRR
	SSR	FSR	SSR	FSR	SSR	FSR		
ASR	51.0	54.5	145	166	44	48	52	260
600°C	48.3	51.7	145	152	48	49	47	300
800°C	39.3	—	131	—	47	—	43	350
1250°C	31.0	43.4	103	131	32	33	36	375

FSR is $2.0 \times 10^{-4} \text{ s}^{-1}$ up to yield point and $1.0 \times 10^{-3} \text{ s}^{-1}$ until break
SSR is $5.56 \times 10^{-5} \text{ s}^{-1}$.

Table II - Analysis of impurities (wt ppm) in the high RRR niobium.

Tableau II - Analyse des impuretés (ppm masse) dans le niobium de RRR élevé.

Lot No.	Metals							Interstitials			
	Al	Si	Ti	Ni	Mo	Ta	W	O	N	H	C
Nb-A1	0	0	1	2	1	364	19	3	4	1	1
Nb-A2	0	0	1	1	1	220	61	2	3	1	0
Nb-B1	0	0	1	1	1	356	17	5	4	1	1
Nb-B2	0	0	0	0	1	222	59	4	5	0	0
Nb-C1	0	0	0	0	0	353	18	1	3	1	1
Nb-C2	0	0	0	1	1	219	59	3	4	1	1
Nb-D1	0	0	0	2	0	359	17	3	4	1	1
Nb-D2	0	0	0	1	1	213	60	3	4	1	1

Table III - Summary of the mechanical properties of reactor grade niobium.

Tableau III - Propriétés mécaniques du niobium de qualité "réacteur".

Sample	RRR	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation %
As received	68	110	226	50
1100 °C 3 h	57	76	183	50
1200 °C 6 h	119	64	165	50
1250 °C 6 h	210	56	120	53

sudden yielding and this disappeared as the material is purified with heat treatments at 1250°C for 6 hours with Ti getter material. This is due to the reduction of interstitial solid solution impurities from the bulk and the increase in RRR value clearly indicates the purification of the reactor grade niobium.

Conclusions

High purity niobium starts exhibiting upper and lower yield stress points after heat treatment at 1250°C for 6 hours with Ti getter material. The reasons for this behavior are not well understood at the present time.

Reactor grade niobium stops exhibiting the characteristic BCC material behavior of upper and lower yield stress points after heat treatment at 1250°C in the presence of Ti as a solid-state getter material. This is due to the reduction of interstitial solid solution impurities from the bulk, which is confirmed by an increase in RRR value to 210, indicating that the reactor grade niobium is further purified.

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