Elasto-Plastic Behavior of High RRR Niobium: Effects of Crystallographic Texture, Microstructure and Hydrogen Concentration

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Abstract. Conventional assessments of the mechanical properties of polycrystalline high RRR niobium via tensile testing have revealed unusually low *apparent* Young's moduli and yield strength in annealed samples. These observations motivated the current investigation of a variety of possible contributors: crystallographic texture, grain size, and impurity concentration. It is shown that the crystallographic textures of a single lot of niobium are essentially unchanged by post-recrystallization anneals at temperatures up to 800°C. Ultrasonic measurements reveal that the elastic response is not degraded by annealing. Rather, the material's extremely low yield point gives the impression of a low elastic modulus during tensile testing.

INTRODUCTION

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. The major impurities in this type of niobium are interstitially dissolved gases such as hydrogen, nitrogen, and oxygen in addition to carbon.

Hydrogen is readily dissolved in niobium, if the natural oxide layer, which forms a diffusion barrier, is defective. Once dissolved, hydrogen diffuses rapidly at room temperature into the bulk at approximately several mm per hour [1]. The concentration of hydrogen tends to be somewhat higher near surfaces, interfaces, and other crystal defects, such as dislocations. At room temperature and concentrations < 6 at % 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 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 K < T < 150 K thus eliminating the precipitation of the ε–phase [3]. 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. This lower strength resulted in the cavities being prone to deform, if they were not handled very carefully, thus affecting both their resonant frequency and field profile.

In addition to lowering the yield strength, it was observed in some lots of material that the Young's modulus was also apparently reduced by a factor of 2 as a result of the hydrogen degassing at 800°C (see Fig 1.) Curiously, material received at other national laboratories exhibited the same anomalous behavior, even without any annealing. Scientists at Argonne National Laboratory reported unusually low apparent elastic moduli in as-received RRR niobium shown in Figure 2 [4]. Based upon these observations, the current study was undertaken involving the following aspects:

i. Since single crystal niobium is anisotropic and a crystallographic texture resulting from the rolling and recrystalization schedules may be responsible for the unusual behavior, texture analyses were performed on samples after five different heat treatments.

ii. Dynamic modulus measurements using the ultrasonic pulse-echo technique were performed to investigate the possibility that the moduli determined by tensile testing were affected by microyielding.

iii. Finally, the results of the above measurements may suggest that some plasticity effect is responsible. Therefore, a metallographic study of the samples was performed to determine the grain sizes after the heat treatments.

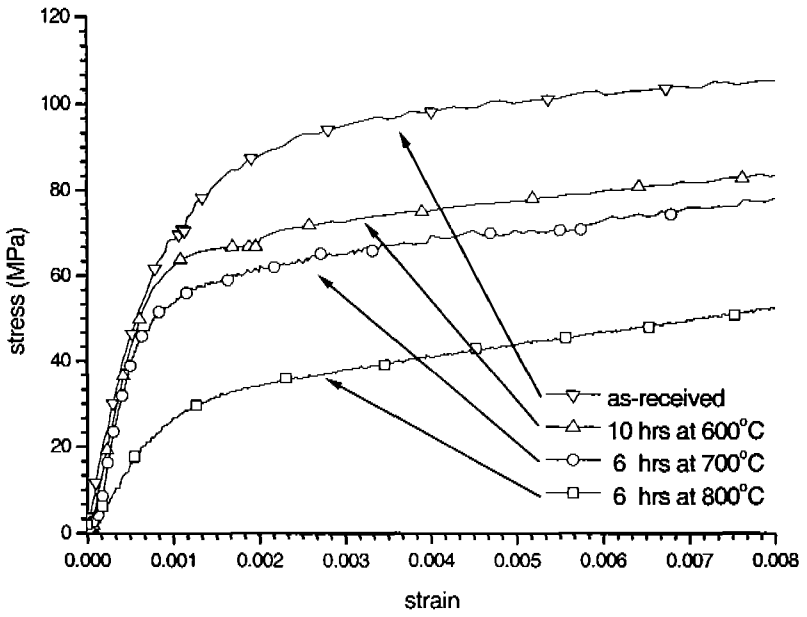

FIGURE 1. Stress-strain plots of the elasto-plastic transition in high RRR Nb subjected to different heat treatments. As-received, 600° and 700°C anneals represent the normal decrease in strength. The 800°C annealed sample also shows a marked decrease in the apparent Young's modulus. Intermediate anneals (e.g. 750°C or shorter time at 800°C) lead to an intermediate behavior.

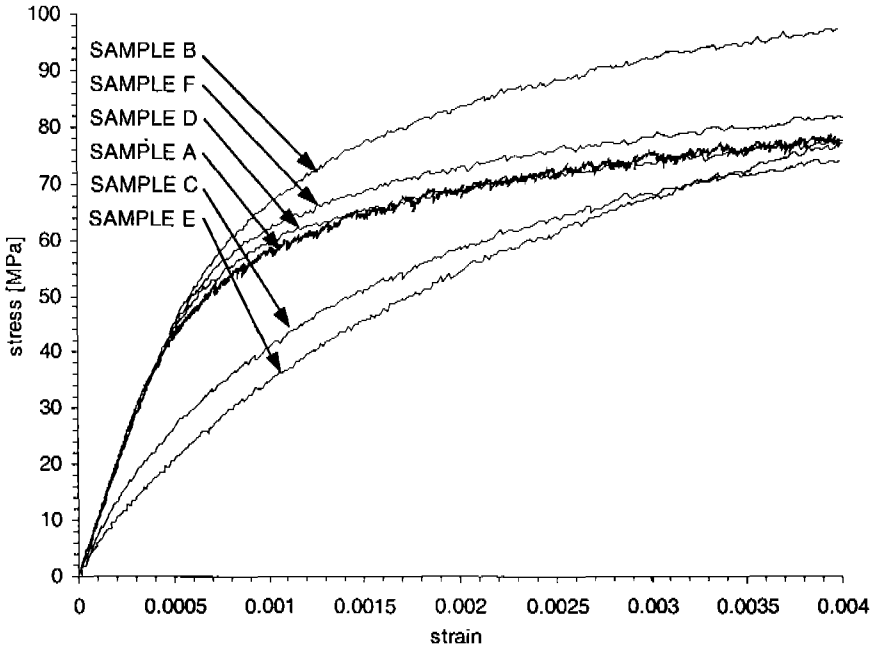

FIGURE 2. Stress-strain plots of as-received high RRR niobium [4], with 2 samples showing same apparent low elastic modulus phenomenon observed in annealed material above in Figure 1.

BACKGROUND

Mechanical properties of high purity niobium were extensively investigated at JLAB during the period 1988 through 1994 and a summary of this database was presented at the DESY TESLA Workshop (March 1995) on Cavity Fabrication Techniques [5]. Most of the work carried out at JLAB was published in various reports and is summarized here for convenience. Room temperature and cryogenic mechanical properties of the as-received CEBAF production niobium including the reactor grade (Cabot) and high RRR niobium (Teledyne Wah Chang, Heraeus and Fansteel) were presented at the 1990 State of the Art Electron Beam Melting and Refining Conference [6].

Extensive cryogenic mechanical properties of as-received and post-purified Teledyne and Fansteel niobium with RRR > 250 and material thickness of 3.175 mm were reported at the 1993 International Cryogenic Materials Conference [7]. Stress-Strain properties of niobium treated under different conditions such as "as received", post-purified at 1400°C and, welded and post-purified at 1400°C, and drastic elongation variation of the post-purified high RRR niobium with BCP and BCP-pressed conditions were incorporated in the first book on RF Superconductivity for Accelerators [8]. Further, thermal and mechanical properties of electron beam welded and heat-treated TESLA niobium were reported in the proceedings of the Sixth workshop on RF Superconductivity organized by the JLAB in 1993 [9].

A careful test program was launched to find the temperature at which the niobium did not change its mechanical properties appreciably, but most of the hydrogen present (contributor to the Q-disease) was expelled. Details of the sample preparation and mechanical properties measurement procedure were described elsewhere [7]. The

accuracy of the strain measurement is ±2%, while the accuracy of the stress is ±1%. The yield strength starts decreasing for all batches of niobium with increasing heat treatment temperature and drops considerably at temperatures higher than 600°C (see Fig. 1). Thus, baking at 600°C seems to be appropriate and there has been no evidence of Q-disease in SNS prototype cavity 4, which was baked at 600°C for 10 hrs.

EXPERIMENTAL

X-ray Diffraction Texture Analysis

A Scintag x-ray diffractometer with a four-circle goniometer and Cu-K_α incident radiation (40 kV, 35mA) was used to measure the crystallographic texture of the niobium samples. The angular positions of the first five Bragg peaks: (110), (200), (211), (220) and (310) were determined with a standard θ-2θ scan from 30-100°. The (110), (200), (211) and (310) pole figures were collected by making a series of continuous phi-scans from 0-360° with the diffracted intensities binned every 5° for a range of chi (tilt) positions ranging from 0-80°, in 5° steps.

The texture data were analyzed using popLA (the preferred orientation package of Los Alamos) [10]. The raw pole figure data were corrected for defocusing using experimental data obtained from a randomly texture standard sample. Since the RRR Nb samples were rolled, the pole figures were found to have orthorhombic symmetry (e.g. Fig. 3). Using a series of three pole figures from each sample, the complete orientation distribution function (ODF) was obtained using the WIMV subroutine of the popLA software. The presented full pole figures were recalculated from the ODF.

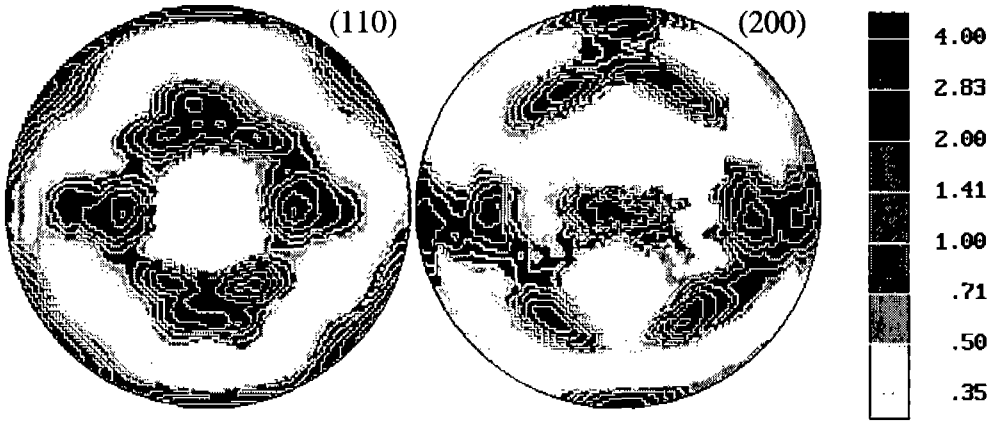

FIGURE 3. Equal area projection (110) and (200) pole figures, with the rolling direction up and the transverse direction left, collected on the as-received WC material. Contours represent multiples of a random distribution on a logarithmic scale. These pole figures exemplify the orthorhombic symmetry present in these cold-rolled and recrystallized materials.

Dynamic Modulus Measurement

A Panametrics Model 5072 Ultrasonic Pulser-Receiver was used in conjunction with a LeCroy 9420 Oscilloscope and 2.25 MHz piezoelectric transducers. Molasses was used as a couplant between the transducers and the samples. Sample thicknesses were measured with a digital micrometer and ultrasonic velocities measured by determining the time-delay between the incident and echo waves reflected from the sample back-surface for a number of echoes. Velocity measurements for both longitudinal and shear waves were necessary to determine the elastic constants C_{33} and C_{44} or C_{55}, respectively. The applicable formulae used are:

$$C_{33} = \rho v_l^2 \tag{1}$$

$$C_{44} = \rho v_{s1}^2 \tag{2}$$

$$C_{55} = \rho v_{s2}^2 \tag{3}$$

where, v_l and v_s are the longitudinal and shear velocities, and ρ is the density. The indices s1 and s2 indicate shears polarized along the rolling and transverse directions, respectively. The wave propagation direction is along the sheet normal direction (or 3) in each case. A constant nominal density of 8.55 g/cc was assumed constant in all calculations, although this assumption is currently under reevaluation. By comparing the values C_{44} and C_{55}, a partial assessment of the material's anisotropy may be made. Assuming the samples are found to be essentially isotropic, Young's moduli and Poisson's ratio may be determined from the values C_{33} and C_{44}, as shown:

$$E_Y = \frac{C_{44}\left(3C_{33} - 4C_{44}\right)}{C_{33} - C_{44}} \tag{4}$$

$$\nu = \frac{E_Y}{2C_{44}} - 1 \tag{5}$$

Optical Metallography

The samples were sectioned for examination transverse to the rolling direction in order to observe any banding or elongation of the microstructure due to processing. The samples were ground using SiC papers through 600 grit. Coarse polishing was performed using 6 μm diamond slurry, followed by intermediate polishing using 1 μm alumina slurry. Final polishing was performed using a procedure of repeated polishing and etching with 0.3 μm alumina and/or 0.05 μm colloidal silica and an etchant containing volumetric ratios 2:2:2:1 of distilled H_2O, HNO_3, HCl and HF.

RESULTS

The measured pole figures have peak intensities of about 4 times random indicating only a moderately strong texture resulting from the cold-rolling and recrystallization processes. The texture strength (as measured by the mean squared intensity value in the ODF) was in the range of 3 for all of the measured samples. Comparison of the features present in the texture data shown in Figure 4 illustrates that there is little

discernable change with annealing. Given that single crystal niobium only has a Zener anisotropy factor of 1.9 [11], these data make it obvious that the anomalous "elastic" behavior induced by annealing can not be explained by changes in texture alone.

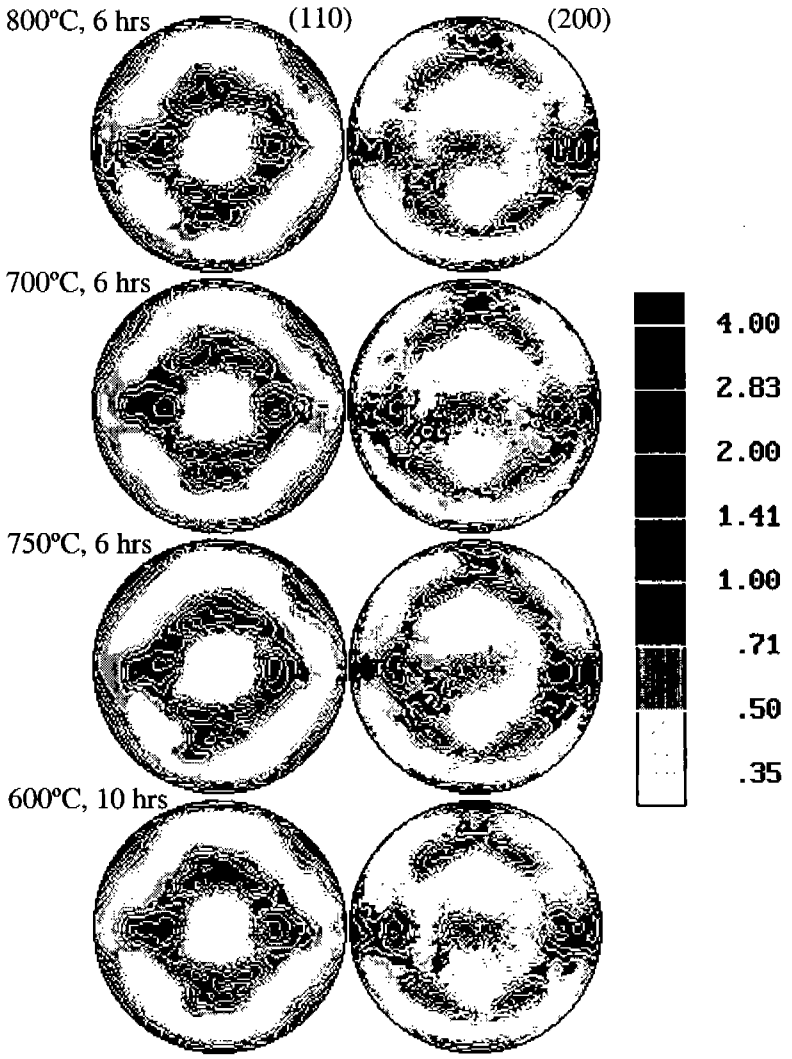

FIGURE 4. Pole figures for WC samples annealed at various temperatures all very similar to the texture of the as-received WC material shown in Figure 3.

Once the texture was shown to be relatively constant with respect to annealing, the textures of subsequently investigated lots were only measured at a single condition (after the 800°C anneal.) Although there is little change in texture with annealing, the current investigation highlights the fact that the texture does vary from one batch to another (Fig. 5). It is suspected that the cross-rolling procedure is not held exactly constant from one batch to another.

As stated above, the birefringence, or ratio of C_{44} and C_{55} shear moduli, provide a means to assess the anisotropy of the material. Since the birefringence was essentially 1.0 in all cases (Table 1), it was possible to determine the Young's moduli, shear moduli, and Poisson ratios of the material. As in the case of the crystallographic texture, the measurements showed that there was little change with annealing. The

average elastic constants are listed in Table 1 for the three lots inspected. The values in the table compare quite well with the standard literature values ranging E = 105.4 – 124.2 GPa [12]. Note that there is much greater variation from lot-to-lot than there is within a lot of annealed samples.

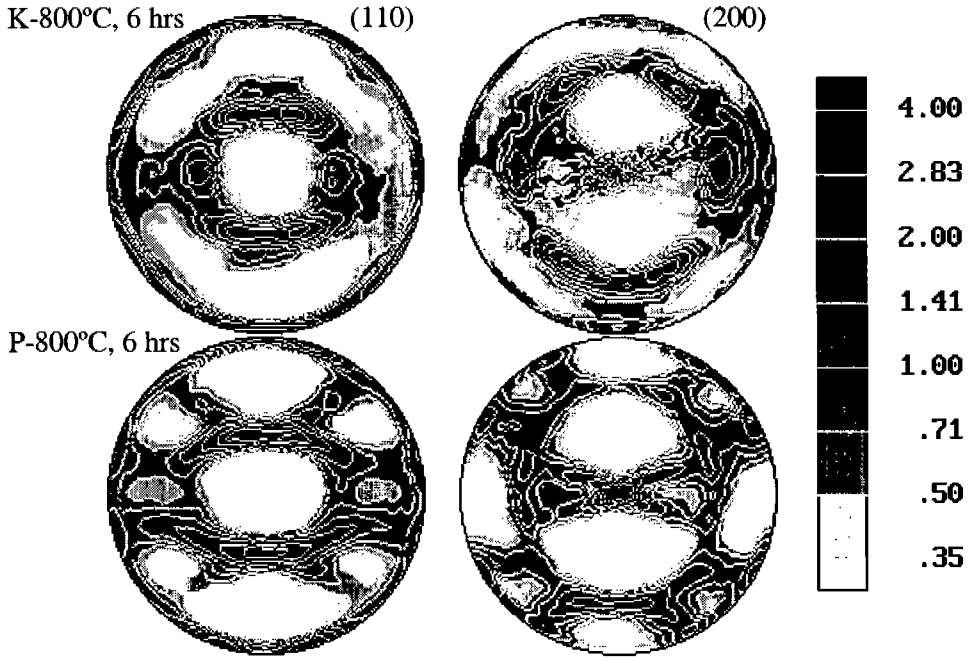

FIGURE 5. Crystallographic texture measurements from the high-purity niobium batches K and P as shown by (110) and (200) full pole figures with the rolling direction up and transverse direction to the left. The distinctions in the textures are most obvious in the (200) pole figures.

TABLE 1. Dynamic moduli measured using ultrasonic velocities.

Material Lot	Birefringence	E (GPa)	G (GPa)	ν
WC	1.01 ± 0.02	108.4 ± 2.4	38.8 ± 1.0	0.40
K	0.99 ± 0.01	114.1 ± 1.2	41.0 ± 0.4	0.40
P	0.98 ± 0.01	108.0 ± 1.0	38.7 ± 0.4	0.40
All	0.99 ± 0.01	110.1 ± 3.4	39.5 ± 1.3	0.40

Hence, it is confirmed that the elastic behavior of the material is normal and, essentially, unaffected by heat treatment. On the other hand, optical metallography showed the grain size to be very sensitive to annealing temperature. Figure 6 shows a typical microstructure from the as-received sample in lot WC and Figure 7 shows the extensive grain growth that occurs with annealing, including the appearance of some exceptionally large grains. One finding that may prove to be important during future studies is the relative inhomogeneity of the grain size. There appeared to be bands of much finer grains than the surrounding matrix located at approximately the quarter-plane of the samples (Figure 8).

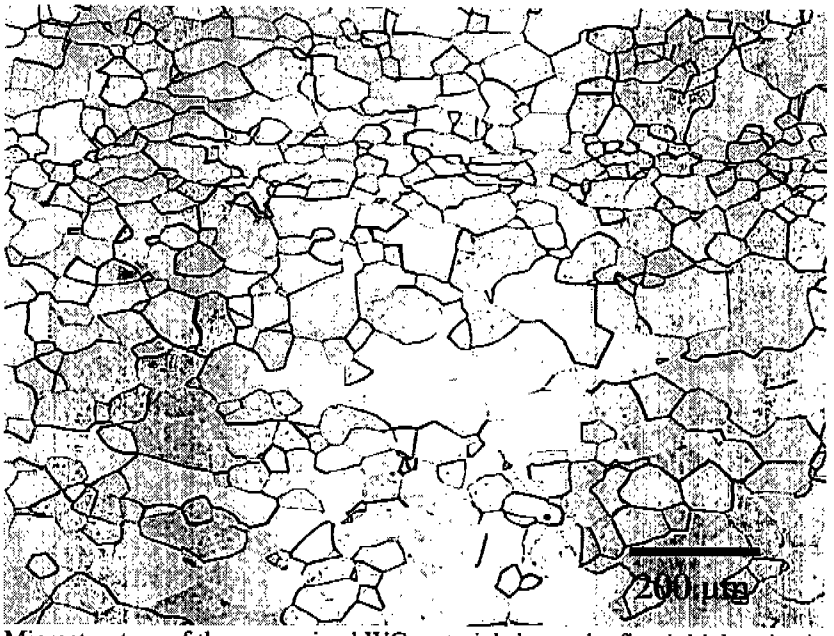

FIGURE 6. Microstructure of the as-received WC material shows the fine initial grain size and the band of smaller grains that could be seen with the naked eye on most of the samples examined.

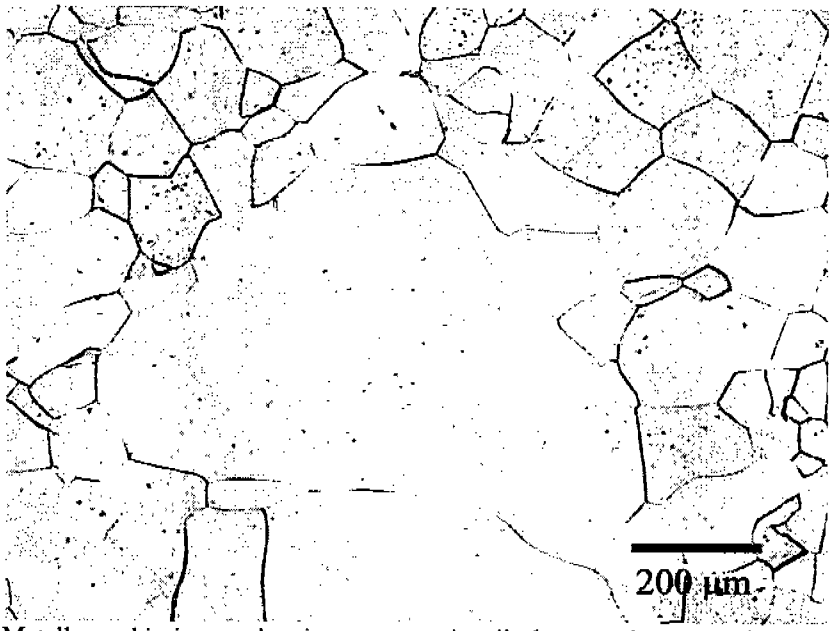

FIGURE 7. Metallographic image showing an exceptionally large grain present in some regions of a WC sample annealed 6 hrs at the highest temperature of 800°C.

Figure 9 graphically illustrates the increase in lineal intercept grain size as a function annealing temperature for samples of lot WC. Also shown are the dynamic modulus measurements, which further indicate that the stiffness of the material is not strongly affected by annealing. However, there is a subtle increase in the elastic moduli observed after the higher temperature anneals, as shown in Figure 9. Figure 10 shows the same trends in grain growth and modulus increase hold for the samples of lots K and P.

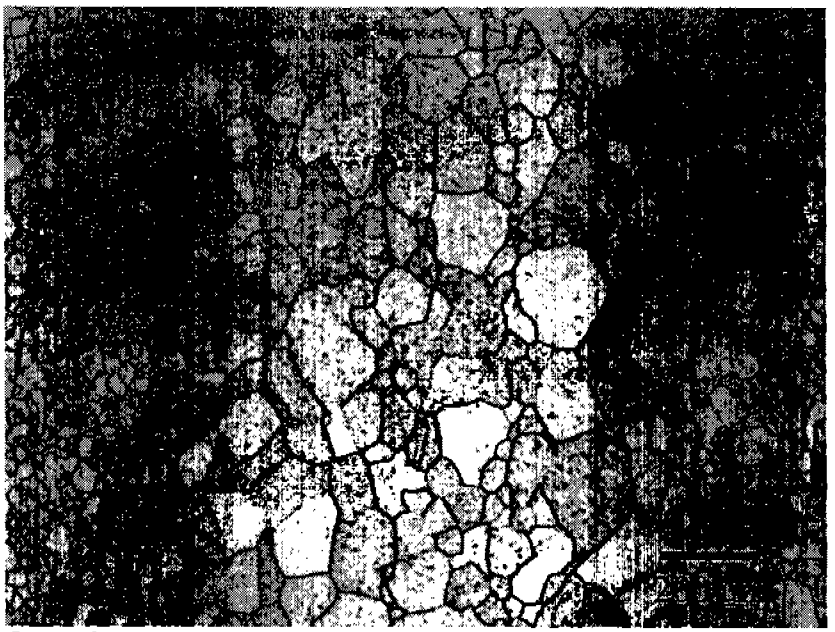

FIGURE 8. Image from a sample annealed 10 hrs at 600°C (lot P) showing typical heterogeneity in these samples' microstructures.

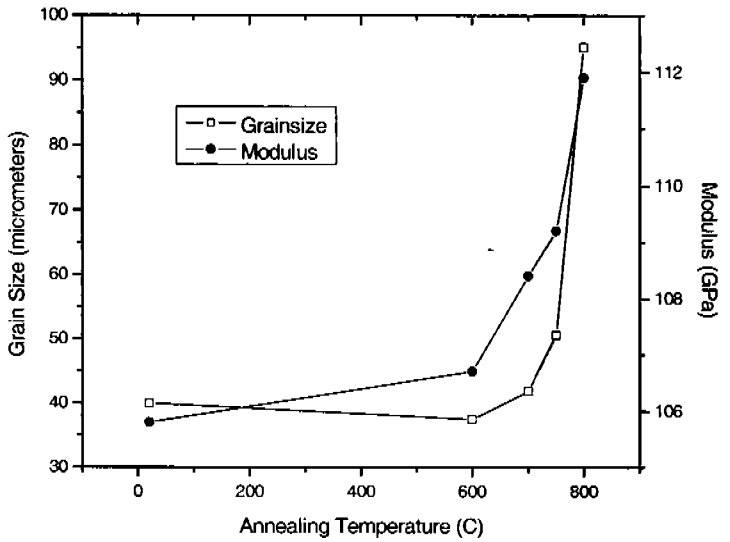

FIGURE 9. Lineal intercept grain size and dynamic Young's modulus as a function of annealing temperature for the high-purity examined during the initial study.

The K batch was found to have both higher elastic modulus and a larger grain sizes than the P batch for all the heat treatments examined. In fact, the K sample annealed at 800°C obtained an average grain size approaching 350 μm. Given the microstructure heterogeneity in these samples (e.g. Fig. 7 and 8), it would not be surprising to find single grains with millimeter dimensions. The batch-to-batch microstructure variation may be integrally strongly linked with lot purity.

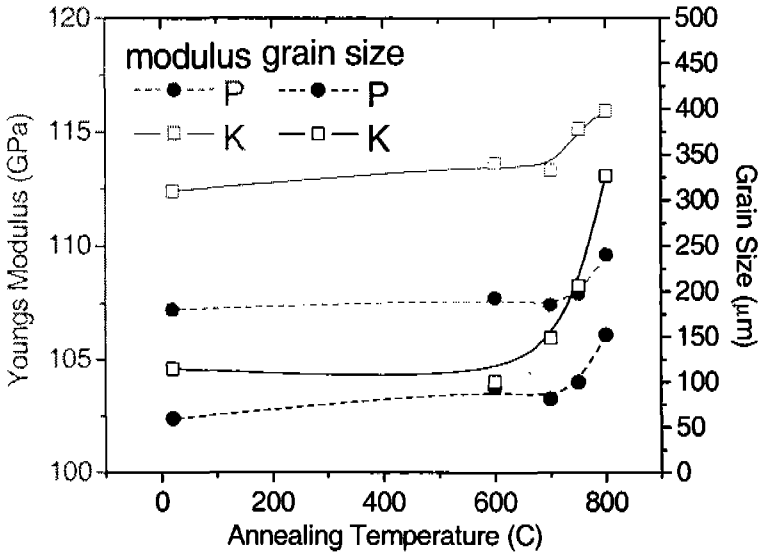

FIGURE 10. Lineal intercept grain size and dynamic Young's modulus as a function of annealing temperature for the high-purity niobium batches labeled K and P.

DISCUSSION

There is no evidence of a dramatically lowered modulus in the heat treated material. In fact, it was later observed that the heat treated material actually exhibited a slight increase in its modulus (see Figures 9 and 10). The anomalous "elastic" behavior indicated by Figure 2 is, in fact, microyielding behavior resulting from the very low yield strength of large grain size high-purity niobium. Unloading studies have shown that the true stiffness of material with a very low apparent modulus is much higher than indicated by the loading curve. Finally, we determined the lineal intercept grain size of the niobium, finding it essentially stable with heat treatment up to 700°C followed by rapid increase in the grain size at higher temperatures (Figs. 9 &10). Since this ultrahigh-purity material essentially derives its strength from a grain size strengthening mechanism, control of the microstructure is paramount.

Analyzing the yield stresses of the samples as a function of their grain size, reveals particular relationship exists. If we assume a Hall-Petch type relation [13,14] all of the data falls on a single line (Fig. 11). This takes some of the mystery out of the "batch-to-batch" variations in strength. It would be good to develop such a master curve from a variety of batches. Note, however, that all three batches examined in this study have similar RRR values, and impurity concentration would be expected to have a strong influence on the strength. Close examination of the Hall-Petch plot shown in Figure 11 shows that there are 3 outliers:

1. the as-received WC sample (97 MPa)
2. the as-received K sample (76 MPa)
3. the 800°C sample (34 MPa)

The reason these samples stand out may be rationalized as follows. It is understood that details of the microstructure can have a strong influence on the materials'

strength. Regarding the high strengths in the as-received material, these samples may not be completely recrystallized. If there is any remaining stored strain energy, this could clearly inflate the yield strength at a given grain size. In the case of the very low strength indicated by #3 in Figure 12, it should be recalled that the samples have significant microstructure heterogeneity (see Figs. 7 & 8) and that a large grained region within the sample would represent a "weakest link." This could make the sample appear weaker than would be expected for the average grain size.

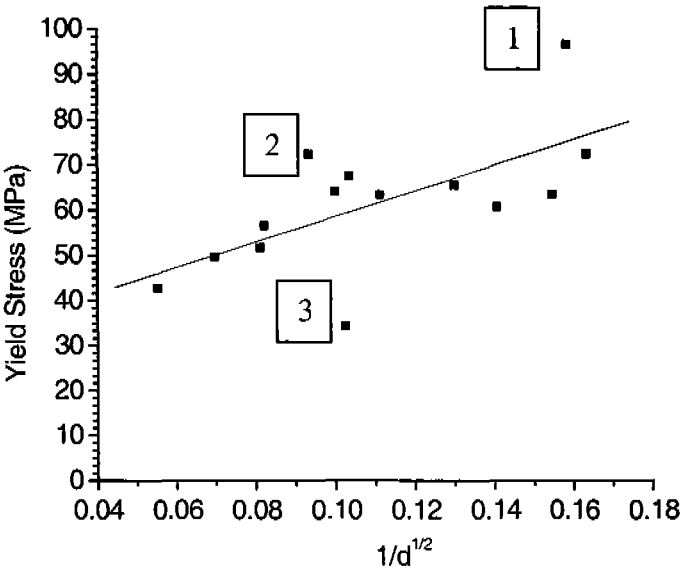

FIGURE 11. Hall-Petch plot of the P, K, and earlier WC samples. This plot shows that the very low yield stress of 5 ksi would be expected for a grain size of about 1mm.

The question remains as to why certain batches of material show the anomalously low yielding behavior and others do not. Further, it is still a question for further investigation as to why the dynamic modulus actually increases with yielding. The fact that the grain size increases at the same time as the moduli is deemed of little importance, since elasticity is a physical property which is relatively structure insensitive (unlike the yield strength [15], obviously.) Yet, the possibility that the annealing of crystal defects is having some effect on the ultrasonic velocities is not ruled out. The simultaneous change in modulus and grain size is suggestive of a change in texture, which could induce a change in the directional modulus, however no change in texture was observed for these samples. Recall that the reason for annealing these samples in the first place is to reduce their interstitial impurity content, namely hydrogen. It may be speculated that the reason for the change in dynamic modulus with annealing may be connected with the concurrent change in impurity concentration. However, there is insufficient data to substantiate such a claim at this time.

Since it is demonstrated that the final mechanical properties of these RRR niobium sheets are strongly influenced by their microstructures, further study into the connection between processing and final microstructure must be undertaken. Such a study should include investigations into the effect of impurity content upon the final

microstructure as well as cross-rolling treatment on the final texture, since texture strongly influences the deep drawing behavior of metal sheets.

SUMMARY

Conventional assessments of the mechanical properties of polycrystalline high RRR niobium via tensile testing revealed unusually low *apparent* elastic moduli and yield strength in annealed samples. These observations motivated the current investigation of a variety of possible contributors: crystallographic texture, grain size, and impurity concentration. It is shown that the crystallographic textures of a single lot of niobium are essentially unchanged by post-recrystallization anneals at temperatures up to 800°C. Furthermore, it is shown that the conventional Hall-Petch strengthening behavior is observed, i.e., grain growth during annealing leads to a significant decrease in strength. Regarding the elastic moduli, dynamic measurements reveal that the elastic response is not degraded by annealing. Rather, it is suggested that the slight *increase* in the elastic moduli with annealing observed using ultrasonic techniques is due to either the elimination of crystal defects or further hydrogen degassing.

ACKNOWLEDGMENTS

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