RRR measurements and tensile tests of high purity large grain ingot niobium

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Abstract. Residual resistivity ratio (RRR) measurements and tensile tests were performed on samples taken from seven high purity large grain niobium ingots produced by CBMM. Test specimens were taken from the top, middle and bottom regions of each ingot. The RRR measurements were performed with a GM cryocooler system and more than 60% of the samples exceeded RRR values of 250. Room temperature tensile tests were performed on samples from the same regions. 17 samples were machined according to ASTM standard test methods for tension testing of metallic material. Tests were performed with an Instron tensile/compression testing machine, and various mechanical properties such as Young’s modulus, 0.2% proof stress, ultimate tensile strength and strain at fracture were measured. For all the samples, the fracture strain exceeds 35% while the ultimate tensile stress is close to 100 MPa. Contents of impurity (N, O, C, H, Ta) of each region of the seven ingots were also measured. These data provide insights for a possible correlation among RRR values, mechanical properties and impurity contents of niobium ingots.

1. Introduction
Superconducting radio-frequency (SRF) cavities are used in modern particle accelerators to efficiently accelerate a beam of charged particles. The power dissipated in the cavity wall is several orders of magnitude lower if superconductors are utilized compared to a normal conductor, thus making superconductors highly efficient in this application [1]. Niobium is the material of choice for making SRF cavities because of its relatively high superconducting transition temperature (~9.3 K), good electrical conductivity and thermal diffusivity, relative abundance and availability, and good formability [2]. Residual Resistivity Ratio (RRR) is a great indicator of the purity and thermal conductivity of a material and the typical RRR value of niobium for RF applications is 200–300 [3]. The RRR value of niobium is measured by comparing the resistivity of niobium at ~10 K (just above its transition temperature) to the resistivity at room temperature [4]. In addition, strength and formability is also essential for the fabrication of SRF cavity, and the improvement of those characteristics allows the cavities to be formed, transported and more easily assembled. The mechanical properties can be provided through tensile test. Those include elastic modulus (E), yield strength (Y), ultimate tensile strength (UTS), and elongation to failure. The yield strength is evaluated using a standard 0.2 % offset strain method to find the 0.2% proof stress (R_p0.2).
In the standard SRF fabrication, high purity niobium sheets with grain size over 50 μm (ASTM ≥5) are selected. The small and uniform grain size of the polycrystalline niobium indicates the good formability and good surface finish [5]. However, the production processes of fine-grain niobium sheet, including hot forging, rolling and annealing, are complicated and expensive. The high RRR material may also experience oxidation and its quality could degrade during the machining. In contrast, the major advantages of large grain niobium ingots are lower cost and simpler machining compared to the standard polycrystalline material [3,6]. Started around 2004, the collaboration between Jefferson Nation Lab and CBMM, a leading global supplier of high purity niobium, has been focusing on machining and testing SRF cavities produced with large diameter, large grain niobium ingot. The results showed that the performance of those cavities satisfy most accelerator requirements, which makes this material very promising for future use [7-9].

In this work, to further investigate the properties of this material, the quality among ingots and within the same ingot at different locations are investigated through measurements of mechanical properties and RRR measurements. Test specimens were taken from the top, middle and bottom regions of seven niobium ingots produced by CBMM. The quality and the mechanical properties of the material was characterized through RRR measurements and tensile tests. The RRR measurements were repeated 10 times for each sample (a total of 23 samples were tested). The samples were tested inside a Gifford-McMahon (GM) cryocooler system (1.5 W at 4.2 K). Tensile tests at room temperature were performed on samples from the same regions as the RRR samples. 17 tensile test specimens were machined according to ASTM E8/E8M standard test methods for tension testing of metallic material. Tests were performed with Instron tensile/compression testing machine, and various mechanical properties including Young’s modulus (E), 0.2% proof stress (R_{p0.2}) and strain at fracture were measured. Contents of impurity (N, O, C, H, Ta, etc.) of regions of the seven ingots were also provided by CBMM to ensure the high purity of the ingots.

2. Sample preparation

Samples were taken from seven ingots with ID: 4162, 4163, 4164, 3782, 3773, 3769, and 3706. The seven ingots were machined by CBMM, and the fabrication process can be found in [8]. During the refining electron beam (EB) melting process in an EB furnace as illustrated in figure 1 (a), the bottom of the ingot is where the solidification starts, and the top of the ingot is where it ends. The RRR samples were removed by diamond disc cutting from the ingots, and chemical analysis was performed at exactly the same locations. The locations where tensile samples were removed are shown in figure 1 (b).

2.1. Samples for RRR measurement

The dimensions of the samples for RRR measurements are 45 mm in length, 2 mm in width and 0.5 mm in thickness. For ingots 4162, 4163 and 4164, four samples were taken from each ingot. Among those samples, 2 samples were taken at the top and bottom positions to ensure the homogeneity of each location. For the other 4 ingots, three samples were taken from top, middle and bottom regions of the ingot. Contents of impurity (N, O, C, H, Ta, etc.) of regions of the seven ingots were also provided by CBMM to ensure the high purity of the ingots.
ingot. No specific cleaning procedure (buffered chemical polishing or electropolishing) was applied onto the sample surface prior to the test, since work presented in [10] indicated that the standard BCP processing for cavity fabrication does not affect the RRR values.

2.2. Specimens for tensile test
The tensile test specimens were taken at the same locations as the RRR samples. A rectangular dog-bone tension test specimen was selected for the mechanical testing of niobium, since it requires less material and it is easier to machine. Standard dimensions for the samples were adopted according to the ASTM E8/E8M standard specifications [11]. The machined tensile test sample with relevant dimensions are shown in figure 2.

2.3. Chemical impurity content
The most important chemical impurity contents (C, N, O, H, Ta) at each location of the ingot where the samples were taken are listed in Table 1 as provided by CBMM. The chemical analysis presents very low level of interstitial impurities. Other low-level impurity contents are W < 50 ppm, Si < 20 ppm, S and Ti <10 ppm; Sn, Al, Fe, Hf, Mo and P < 5 ppm; V, B, Be, Cd, Co, Cr, Ni, U and Zr < 1 ppm. The Tantalum content varies from less than 100 ppm to almost 1700 ppm between inots.

Table 1. Major Impurity Contents for 17 Samples

| Region | Ingot | 4162 | 4163 | 4164 | 3706 | 3769 | 3773 | 3782 |
|--------|-------|------|------|------|------|------|------|------|
| H (ppm) | Top   | 3    | 2    | 2    | <2   | <2   | <2   | 2    | 2    | 4    | 2    | <2   |
| N (ppm) | Top   | 5    | 10   | <5   | 8    | 6    | 10   | 5    | 6    | 8    | 13   | 31   | 5    | 7    |
| O (ppm) | Mid   | 6    | 10   | 15   | 10   | 13   | 11   | 17   | 11   | 13   | 20   | 22   |      |
| C (ppm) | Mid   | 10   | 14   | 6    | 5    | 10   | 3    | 6    | 5    | 10   | 11   | 20   | 22   |      |
| Ta (ppm) | Bot  | 81   | 255  | 918  | 1278 | 1697 | 1670 | 775  | 568  | 657  | 1161 | 1292 | 1223 |      |

3. RRR measurement
In this section, the measurement apparatus utilized for the RRR measurements and the results are discussed in detail. The RRR measurements were performed applying a DC-method, and the resistance of the sample was obtained by a standard 4-point measurement. The RRR value in this work is defined as the ratio of the sample resistance at room temperature (298 K), and the resistance at 9.5 K with no background magnetic field, as discussed in [3]. Note that another method defines RRR to be the ratio of resistance at room temperature and the one at 4.2 K [3]. In this method, the resistance at 4.2 K is extrapolated from the one at 9.5 K [3]. The RRR values of the samples reported in this work are roughly 10% lower than the extrapolated RRR values. Considering niobium is not a solder-friendly material, electrical
contact between sample and wires to measure the voltage across the samples was achieved through mechanical contact instead of soldering. The measurements were performed on a custom designed sample holder, and a GM cryocooler was utilized as cooling system.

3.1. Sample holder design and procedures of RRR measurement

The illustration of the sample holder is shown in figure 3 and a picture of the fully assembled probe is shown in figure 4. The base of the sample holder was assembled from sandwiching a G10 plate with two identical copper plates. The copper plates were wrapped with a thin non-adhesive Kapton tape to be electrically insulated from the samples (figure 3). The copper plates, due to their excellent thermal conductivity, serve as heat sink to maintain a homogeneous temperature of the niobium samples. Current leads and voltage taps are secured through mechanical contacts on pieces of G10 and copper (exploded view in figure 3). The copper block was fixed on the G10 piece with screws. Good electrical and mechanical contact between the sample and the current leads and voltage taps was established by tightening bolts and nuts shown in the figure. Three samples were mounted on each side of the sample holder and wired in series so that six samples can be tested in one cool down. After the samples were mounted, and the sample holder was assembled onto the probe, the resistance was measured at room temperature. The probe was then placed inside the cryocooler to be cooled down to 9.5 K for another resistance measurement of the samples.

During each resistance measurement, a staircase current sweep from -200 mA to 200 mA with an increment of 50 mA was performed, with 20 voltage data points recorded at each step. Each resistance measurement was repeated 10 times. This method yields an uncertainty of less than 3% for each RRR measurement.

3.2. Results of RRR measurements

For ingots 4162, 4163 and 4164, 2 samples were taken at the bottom and the top of the ingots to investigate the homogeneity at the same location. As shown in figure 5, the two samples taken at the same at location have similar RRR values. The measurements also agree with the reference provided by CBMM. However, samples taken at different regions of the ingot have different RRR values. For example, sample 4162 Top has RRR of >500, while the RRR of sample 4162 bottom is close to 300.

This behaviour was also observed from the samples taken from ingots 3782, the RRR value at top is >500, and <300 at the bottom. This variation along the ingot is due to the fact that during the refining melting process in an EB furnace, as shown in figure 1 (a), the starting solidification point is on the bottom of the ingot and it ends at the top of the ingot. Normally the pressure inside the melting chamber
gets better (decrease) along the melting. At the beginning inside the furnace, some traces of gases (especially O, N and H) can be found, and they gradually decrease along the melting time. Generally, this allows better refining process of the ending point of process, which is at the top of ingots. This can also be observed from the impurities of Top and Bottom regions of ingot 4162 listed in Table 1.

The RRR values of the samples from the seven ingots are listed in Table 2. The RRR values of 11 out of 17 samples exceed 250, and only 2 samples’ RRR values are lower than 200. This indicates that the overall quality of the ingot is good. The major difference impurity content between the ingots is the Ta content, and test result shows that with high Ta content (> 1000 ppm), the RRR can still exceed 200. Since the impurities of C, N and O vary significantly among those samples (from 2 to 20 ppm as shown in Table 1) and they have much more impact on the RRR values than Ta, it is hard to conclude the correlation between RRR and Ta contents from these data.

4. Tensile tests
In this section, the results of tensile tests are discussed in detail. 17 samples were taken from seven ingots, and a picture of a representative sample and its dimensions are shown in figure 2. Tensile tests were performed on an Instron 5500R tensile/compression testing machine, with a strain rate of 1% strain per minute. The strain was recorded by a pair of extensometers. The mechanical properties including Young’s modulus (E), 0.2% proof stress ($R_{p0.2}$), UTS, and strain at fracture were measured through the tests. The fracture profiles of the samples are also presented and the potential correlation between strain at fracture and RRR values is discussed. According to the illustration on how the samples were cut shown in figure 1 (b), there is a great probability that these tensile samples contain some grain boundaries (samples were not cut trying to avoid grain boundary). Studying the crystal orientation was beyond the scope of this work but future work will be conducted to the tested samples to understand how the grain boundaries and crystal orientations might have affected the rupture.

4.1. Stress-strain behaviour
The work hardening behaviour and the elastic range between samples are very different at low strain, and 16 out of 17 samples started to yield under 0.2% strain. Five stress-strain curves are shown in figure 6 to illustrate the behaviour of the samples. The offset in stress at 0% strain is due to the residual stress when gripping the sample and it is small compared to the overall stress measured. 3 out of 17 samples started yielding at or slightly below 0.05% strain, with stresses less than 50 MPa. To compare all the samples, the elastic modules were defined as the slope of the linear fitting in the strain range from 0% to 0.05%. The Young’s modulus of each sample was used to evaluate the 0.2% proof stress ($R_{p0.2}$) with an offset in strain of 0.2%.

For typical ductile materials, once the material is in the plastic region, the speed of the strain applied can be increased to speed up the test. A slower rate during the elastic phase is needed to record good values for the linear region, but a faster rate in the plastic region typically does not impact the material

![Figure 6. Stress-strain curves for 5 sample in strain range from 0% to 0.2%.](image_url)

![Figure 7. 5 typical stress-strain curves up to fracture of the measured niobium samples.](image_url)
properties. While testing sample 4162 Top and Bottom, the strain rate was increased to 5% strain per minute when the strain reached 10% but a sudden increase in stress (~5 MPa) was observed when the strain rate was changed. This behaviour has been observed before as reported in [12] and it is considered detrimental in reporting the mechanical properties values. Therefore, following those first two samples, it was decided to apply a uniform strain rate of 1% per minute for the entire duration of the test and for all the samples despite significantly increasing the time to perform one single test. Five typical stress-strain curves up to fracture obtained for the niobium samples are shown in Figure 7. The behaviour observed fall within the category of single-crystal niobium as discussed in [13,14], with the most notable characteristic being the rapid increase and a peak in stress at less than 5% strain.

4.2. Mechanical properties and fracture profiles

The strain at fracture varied from less than 40% to close to 90% among the samples, and different fracture profiles were observed. Three typical fracture profiles are shown in Figure 8. The rupture of sample 4162 Top shown in figure 8.a has the longest %elongation at fracture, close to 90%. An angle close to 45⁰ is observed at the location of fracture between two pieces. This shear fracture is very similar to the result of a mono-slip behaviour in single crystal [15]. The shear fracture in figure 8.b has lower %elongation, and the angle formed at the place it fractured is close to zero (flat line of separation). The third fracture profile shown in figure 8.c has one of the lowest %elongation of all the samples, and the chisel-edge fracture can be observed on the side. The fracture profiles reported are possibly affected by both grain boundaries and crystal orientations. At this point, the mechanism of the ruptures is not well understood, and it is beyond the scope of the work presented here but it will be investigated in the future through the tests of additional samples.

The detailed mechanical properties, including E, R_p0.2, UTS, and strain at fracture, combined with the RRR values and Tantalum impurity content are shown in Table 2. Note that the RRR value for samples from ingots 4162, 4163 and 4164 are the average of two measurements. As shown in figure 9, for the 6 samples taken from ingots 4162, 4163 and 4164, there is a rather strong correlation showing that higher RRR value samples experience higher elongation. Higher RRR niobium indicates lower content of interstitial elements (C, N, O and H). Consequently, the material will have fewer barrier to block the dislocations slipping in the material matrix and therefore higher elongation is expected. If all the 17 samples are considered (figure 10), the correlation becomes weaker. The weaker correlation could

![Figure 8. Three typical fracture profiles of the tensile test specimens. (a) The rupture of sample 4162 Top has the longest %elongation at fracture, close to 90%. This shear fracture is mainly a result of a mono-slip in the crystal. An angle close to 45⁰ is observed at the location of fracture between two pieces. (b) Sample 3773 Middle has lower %elongation of 67%, and the angle formed at the place it fractured between two pieces is close to zero. The shear fracture can be observed on the cross section at fracture. (c) Sample 4163 Bottom has one of the lowest %elongation of 37.7%, and the chisel-edge fracture can be observed on the side face. [14]](image-url)
be caused by different grain orientation of the different samples. In addition, there is no obvious correlation observed between strength (yield stress, UTS) and Ta contents. More study on the crystal orientation will be needed to further interpolate these data.

Table 2. Summary of mechanical properties, RRR and Ta impurity for all the samples tested

| Ingot | Region | UTS (MPa) | Rp0.2 (MPa) | E (GPa) | %Elongation | RRR | Ta (ppm) |
|-------|--------|-----------|-------------|---------|-------------|-----|----------|
| 4162  | Top    | 115       | 93          | 65      | 92.0%       | 594 | 81       |
|       | Bottom | 94        | 87          | 143     | 52.0%       | 289 | 255      |
| 4163  | Top    | 99        | 82          | 73      | 36.8%       | 150 | 918      |
|       | Bottom | 93        | 86          | 94      | 37.7%       | 231 | 1278     |
| 4164  | Top    | 136       | 124         | 75      | 51.7%       | 360 | 1697     |
|       | Bottom | 101       | 88          | 127     | 39.2%       | 197 | 1670     |
|       | Top    | 107       | 105         | 94      | 37.4%       | 223 | 775      |
| 3706  | Middle | 95        | 87          | 114     | 51.4%       | 327 | 568      |
|       | Bottom | 95        | 90          | 83      | 40.0%       | 325 | 657      |
|       | Top    | 84        | 77          | 89      | 51.7%       | 294 | 1161     |
| 3769  | Middle | 116       | 71          | 87      | 57.8%       | 307 | 1292     |
|       | Bottom | 104       | 73          | 67      | 43.9%       | 268 | 1223     |
|       | Top    | N/A       |             |         |             |     |          |
| 3773  | Middle | 99        | 85          | 86      | 67.5%       | 207 | 1313     |
|       | Bottom | 96        | 74          | 72      | 48.0%       | 209 | 1501     |
|       | Top    | 99        | 66          | 86      | 89.2%       | 522 | 85       |
| 3782  | Middle | 91        | 66          | 59      | 62.9%       | 299 | 93       |
|       | Bottom | 116       | 84          | 68      | 49.6%       | 258 | 158      |

5. Conclusions

RRR measurements and tensile tests were performed on samples taken from the top, middle, and bottom positions of seven high purity large grain niobium ingots produced by CBMM. High RRR values (15 out of 17 samples exceed 200) were obtained from the measurements indicating the good quality of the samples. The RRR values are similar at the same location, however vary along the ingot (from ~300 to >500 for ingot 4162 bottom to top). The variation can be explained by the change of impurities during
the refining melting. The major different impurity content between the ingots is Tantalum content, however, no obvious correlation with RRR values or strength was observed. Mechanical properties including Young’s modulus, 0.2% proof stress, UTS, and strain at fracture of the specimens taken at the same location as the RRR samples were obtained through standard tensile tests. The results show that the %elongation of all the samples exceed 35% and the greatest one is close to 90%. Three types of fracture profiles are observed from these measurements, and the profiles are similar to the rupture profiles of single crystal reported in literature. Samples with high RRR values experience higher elongation. The 6 samples from ingot 4162, 4163 and 4164 show a good correlation with a linear fit with R² value of 0.95. If all 17 samples are considered, the correlation becomes weaker (R² value of 0.70). The reason of this weaker correlation may due to the grain orientation of the samples. The effects of crystal orientation of the samples were beyond the scope of the work presented here but it will be investigated in the future through more tests and etching of the ruptured sample surfaces.

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