Physical Properties and Structure of Large Grain/Single Crystal Niobium for Superconducting RF Cavities*

A. Ermakov¹, I. Jelezov¹, X. Singer¹, W. Singer¹, G.B. Viswanathan², V. Levit², H. L. Fraser², H. Wen¹, M. Spiwek¹
¹ Deutsches Electronen-Synchrotron DESY, Hamburg, Germany
² Center for the Accelerated Maturation of Materials
Department of Materials Science and Engineering
The Ohio State University, Columbus, Ohio, USA

E-mail: alexey.ermakov@desy.de

Abstract. The R&D program on superconducting cavities fabricated from electron beam melted large grain/single crystal (LG/SC) niobium discs explores it’s potential for production of approximately 1000 cavities for the European XFEL. Thermal, electrical, mechanical properties, crystal orientation and structure are investigated with the aim to make the fabrication procedure more efficient. In opposite to fine grain niobium the thermal conductivity of LG/SC has a pronounced maximum at 2K. Calculation found a correlation between thermal conductivity enhancement and phonon scattering at the grain boundaries. Detected enhancement is very susceptible to plastic deformation that can cause the complete elimination of the low temperature peak. The final annealing at 800°C of cavities made from large grain niobium is necessary for hydrogen outgassing, as well as for the thermal conductivity enhancement due to stress relaxation and recovery of crystal defects introduced at the cavity fabrication. The effects of annealing temperature up to 1200°C, heating rate, and holding time on the structure recovery after rolling are also established. Total elongation at the uniaxial tensile tests for LG is very high (50 - 110%) and depends significantly on the load direction, because only very few grains are in the gage length. The elongation after fracture by bi-axial testing (bulging test) for LG is lower (<15%) yet sufficient for deep drawing of half-cells. Metallographic investigation of and electron beam welding tests on, niobium single crystals show that an appropriate disc enlargement and annealing can be done without destruction of the single crystal. These tests showed that a cavity can be produced without grain boundaries even in the welding area. On base of the results a fabrication method of single crystal cavities is proposed.

1. Introduction
The main aim of the R&D DESY program is to find the reliable and cost effective way to fabricate and treat the approximately 1000 cavities for the XFEL project. An encouraging cavity fabrication approach was proposed at Jefferson Lab. High purity niobium sliced directly from EB melted large grain ingot was used instead of niobium sheets. Several single cell cavities deep drawn and EB welded demonstrated very promising performance with accelerating gradients up to 35 MV/m by only
chemical polishing of cavity inside BCP. Similar results were recently observed at DESY on a three 9-cell cavities. Large grain option could be a cost effective solution because the long chain of fabrication steps from ingot to Nb sheet will disappear.

Even more exciting is the single crystal (grain boundary free) option. Its very high potential is already demonstrated at JLab on a cavity of 2.2 GHz frequency (Low Loss LL shape) fabricated from two rather small single crystal discs [1]. It seems that in short term the industry will not be in position produce single crystal of dimensions sufficient for ILC cavity shape (TESLA, LL or Reentrant RE). DESY investigation has shown that the definite enlargement of the discs diameter is possible without destroying the single crystal structure [2]. In addition it becomes possible to produce the cavity grain boundary free even at the welding area by special preparation and welding. An appropriate annealing allows the outgassing of hydrogen and stress relaxation of the cavity without destroying of the single crystal. A fabrication method of cavities of ILC like shape was proposed. Two single crystal single cell cavities were build at the company and reached an accelerating gradient of ca. 40 MV/m. The single crystal option could lead to an essential improvement in the cavity technology not only regarding Q(Eacc) performance. It seems that the quality control and treatment procedure can be also significantly simplified. This paper is dedicated the investigation of the thermal, mechanical properties and structure of the Nb large grain/single crystal sheets in order of better understanding of details and the concealed attributes.

2. Experimental procedure

a. Preparation of the samples for thermal conductivity, tensile and bulging tests.

The samples were cut out from large grain Nb disc of RRR300 purity by water cutting and additionally milling at cutting edges. The samples for uniaxial tensile test have marked considering the orientation. For bulging test the round samples included three large grains. The samples for thermal conductivity measurements are also cut from the same material in the form of bar with dimensions 2x2x80 mm.

b. Preparation of the samples for structure deformation investigation (rolling).

Cube of coarse grain niobium (figure 1) was cut into single crystal slices with a large plane oriented by XRD Laue method parallel to (001), (011), or (111). The rectangular samples of 5-10 mm thick were rolled at room temperature either in one or in two mutually perpendicular directions of <110>.

General height reduction during rolling was of 5% per pass and final thickness was obtained after 5-10 passes. After rolling in a strain range 25 -50% the samples were cut into pieces and annealed in vacuum for 3 hours at the temperatures 800-1200°C. The microstructure and orientation changes in the initial single crystals were analyzed by means of TEM, SEM, OIM, optical microscopy and XRD.
3. Thermal Conductivity of Large Grain/Single Crystal Niobium

Bulk niobium cavities made from large grain or single crystal niobium may benefit from the thermal conductivity enhancement at around the running temperature 1.8K due to reduction of the scattering of phonons on grain boundaries. The total heat conductivity of the superconducting metal is obtained by adding the electron term and the phonon term.

\[
\lambda_s(T) = R(y)\left[\frac{\rho_{295K}}{L_0 \cdot RRR \cdot T} + aT^2\right]^{-1} + \left[\frac{1}{D \exp(y)T^2} + \frac{1}{BT^5}\right]^{-1}
\]  

(1)

\(T\)-Temperature, \(RRR\)-residual resistivity ratio, \(l\)-phonon mean free path. The fitting for high purity niobium coefficients are given in work [3].

It is to expect that contribution into thermal resistance from scattering of phonons on the grain boundaries are disappeared or will be significantly reduced due to reduced number of grain boundaries for large grain or missing of them for single crystal. Calculation of thermal conductivity using the formula for \(\lambda_s(T)\) and as the phonon mean free path the sample width of ca. 3 mm (instead of grain size for polycrystalline material normally ca. 50\(\mu\)m) can be seen in figures 2-3. Phonon peak is clearly pronounced.

The thermal conductivity of a series of fine grain (polycrystalline), large grain and single crystal niobium samples were measured at low temperatures. The experimental results (figures 2-3) are emphasis pronounced phonon peaks on large grain and single crystal heat treated at 800°C niobium samples produced by W.C. Heraeus (figure 2), while no ‘phonon peak’ on fine grain samples independently on RRR value are observed. The dependence of the phonon peak on crystallographic orientation was not dedicated.

No “phonon peak” was observed on a large grain niobium sample from Ningxia. Additional crystallographic structure investigation has shown that NINXIA large grains consist of many small powders like crystals.

Further investigation has shown that the phonon peak may be destroyed by stress inside the sample due to plastic deformation. Already a small plastic deformation of 8.5% has made the phonon peak totally disappeared (figure 3). Similar results can be also found in Reference [4]. It implies that the final cavity made with large/single crystal niobium might not benefit from the thermal conductivity enhancement due to the plastic deformation during cavity fabrication (deep drawing of half cells). Nevertheless final annealing at ca. 800 °C might be helpful not only for outgassing of the hydrogen but also for the stress relaxation.

![Figure 2. Thermal conductivity of fine grain, large grain and single crystal niobium (mfp: phonon mean free path)](image)

![Figure 3. Plastic deformation influence on thermal conductivity of single crystal niobium.](image)
4. Mechanical Properties: Tensile Test; Bulging Test

Crystallographic orientation of large grain niobium samples used for tensile and bulging test can be seen in figure 4. The uniaxial tensile test was performed on three different oriented Nb large grain samples. The results on tensile test demonstrate a significant anisotropy of the elongation at break (figure 5). The samples No. 2 and No. 3 shows the total elongation close to 60%. The sample No.1 cut out from the grain with plane (100) demonstrate a 2 times larger elongation at break (>100 %) compare to sample No. 2 located in the same grain but with angle of about 45 degree to the long axis of sample No.1. The sample N3 has the grain boundary between the grains separated the (111) and (110) planes.

A hydraulic bulge tests were conducted to evaluate the niobium properties compare to the uniaxial tensile test. Figure 6 shows the scheme of bulging test equipment. This method allows getting the true strain-stress characteristic of the material. The values of the stress $\sigma$ and the strain $\varepsilon$ at zenith can be found with help of the formulas

Figure 4. Orientation of used large grain niobium and samples cut for tensile and bulging test

Figure 5. Elongation tests results for 3 single crystal samples with different orientations.

Figure 6. Scheme of the bulging device

Figure 7. Biaxial bulging test results on large grain Nb sample. Curve for polycrystalline sample shown as reference
\[ \sigma = \frac{pr}{2t} \quad \text{and} \quad \varepsilon = \ln \frac{t}{t_0} \]  

The pressure \( p \), radius of the curvature \( r \) and thickness \( t \) in zenith of the sample are measured during the deformation procedure with curvature sensor and ultrasonic device. During the bulging test a disc with 130 mm diameter is bulged into a die with 100 mm inner diameter. Figure 7 shows results of biaxial bulging tests. Percentage elongation after fracture by biaxial deformation for large grain is significantly lower (<15%) compared to tensile test results. The rupture takes place on grain boundary close to the center of the disc.

5. Structure Investigation of Single Crystal Behavior after Rolling and Annealing.

**Figure 8.** TEM images and selected area diffraction patterns of niobium single crystal after cross rolling (001) <110>, 50% reduction.

**Figure 9.** TEM images and selected area diffraction patterns of niobium single crystal after cross rolling (001) <110>, 50% reduction, annealing for 3 hours at 800°C (left); at 1200°C (right).

Niobium single crystal plates oriented (001), (011), (111) were rolled at the room temperature either in one or in two mutually perpendicular directions of <110> within a strain range of 25-50%, then annealed in vacuum for 3 hours at the temperatures 800-1200°C. TEM foils were cut from the deformed or deformed and annealed samples parallel to the rolling plane. SEM, OIM, XRD and optical microscopy were applied to the both: rolling plane and cross section perpendicular to the rolling direction.

Dislocation structure of the single crystal (100) after rolling in direction <110> with strain 50% is shown in figure 8. Two mutually perpendicular slip systems are operating. Dislocation density is high in general especially in the narrow bands parallel to the slip planes (figure 8). Selected area diffraction (S.A.D.) show TEM foil plane, which was cut parallel to the rolling plane, is (001), i.e. does not change at cross rolling.

After annealing at 800 °C and 1200 °C of deformed crystals oriented (100) dislocation density goes down (figure 9), however orientation of the rolling plane does not change. Neither cell nor subgrain formation is observed. The rolling plane orientation (001) does not change indicating no recrystallization.
The Inverse Pole Figure shows that single crystals rolled with 50% deformation maintain orientation stability (001) after 1200 °C annealing (figure 10). Orientation map of the cross section perpendicular to the rolling direction of [110] corresponds to color map green corner <101> of stereographic triangle (figure 10).

![Figure 10. Orientation stability of Nb SC (001) after 50% cross rolling and annealing at 1200 °C. Orientation map of the cross section perpendicular to the rolling direction of [110].](image)

That result is in a good agreement with both: TEM and etch pits data indicating luck of recrystallization at these conditions. There was no recrystallization found after annealing for 3 hours at the temperature 1200 °C of all single crystals rolled in (100) and (110) orientations. It means that for recrystallization should not occur during annealing either after lower strain, or annealing for the shorter time, and/or at lower temperature. These data were supported by SEM observation of the etch pits, similar to given below for (111) crystals.

![Figure 11. Recrystallization in Nb single crystal (111) after 50% rolling and annealing at 1200 °C for 3 hours. Cross section perpendicular to the rolling direction does not match initial orientation of [110] indicating the new recrystallized grains.](image)

Both OIM and SEM show the recrystallization after annealing at 1200 °C crystals rolled in (111) orientation (figure 11). The same crystals overcome dislocation recovery only during annealing at 800°C (figure 12). The same rolling plane orientation all over the sample before deformation as well as after annealing at 800°C indicates luck of recrystallization.
Major problem of recrystallization prevention is how to avoid external RX nucleation related to the surface defects, inclusions, rolling non-uniformity etc.

**Figure 12a.** SEM image of etch pits on the rolling plane (111) of niobium single crystal before rolling. 6 fold symmetry indicates plane of \{111\} type.

**Figure 12b.** SEM image of etch pits on the rolling plane (111) of niobium single crystal after rolling in (111) [110], 50% reduction, annealing for 3 hours 800ºC.

6. Electron Beam Welding of Niobium Single Crystals

Further investigations are focused on the issues of electron beam EB welding of single crystals. It turned out that two single crystals would grow into one single crystal, if the crystallographic orientations were matched at the EB seam.

**Figure 13a.** Electron beam welding connection of two single crystals without regarding of crystals orientation (the grain boundary is pronounced)

**Figure 13b.** Electron beam welding connection of two single crystals after [assembling in such a way that] matching their orientations [of two single crystals are identical] (the grain boundary is absent)

The results of metallographic analysis of the cross section can be seen in figures 13a, b whereas unmatched orientations produce a pronounced grain boundary (figure 13a), matched orientations of both single crystals grow together without interface (grain boundary free) (figure 13b). The orientations of the two matched single crystal samples after EB determined by means of Laue back scattering could be seen in figure 14. As figure 14 demonstrates, the same crystallographic
orientations of both primary samples (left and write) were preserved during EB welding. The EB welding connection seam has the same orientation too.

7. Summary
The thermal conductivity results shows pronounced phonon peaks at low temperature on large grain and single crystal niobium samples while no peaks for fine grain samples with similar RRR values have been observed. The phonon peak can be easily destroyed already by small plastic deformation of 8.5 %.

Uniaxial tensile test and biaxial bulging tests on the LG/SC Nb samples show the different results. The tensile test shows the anisotropy of elongation depending on the crystallographic orientation, though independently on crystallographic orientation the elongation remains high (> 55%). In opposite the biaxial bulging tests shows only 11-12 % elongation at break. The fracture takes place close to grain boundary.

Niobium single crystals of (001) rolled up to 50% could keep their orientation after annealing at the temperature interval 800-1200°C. Dislocation structure recovered during annealing without cell or subgrain formation, which prevents nucleation of new grains (RX nuclei). Single crystals of rolling plane of (111) deformed with the strain of 50% have recrystallized during annealing at temperature 1200°C, but have just dislocation recovery at the lower temperatures.

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