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Titled

“Fine Grain Nb Tube for SRF Cavities”

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Abstract

Superconducting radio frequency (SRF) cavities used in charged particle linear accelerators, are currently fabricated by deep drawing niobium sheets and welding the drawn dishes together. The Nb sheet has a non-uniform microstructure, which leads to unpredictable cavity shape and surface roughness, and inconsistent "spring-back" during forming. In addition, weld zones cause hot spots during cavity operation. These factors limit linear accelerator performance and increase cavity manufacturing cost. Equal channel angular extrusion (ECAE) can be used to refine and homogenize the microstructure of Nb tube for subsequent hydroforming into SRF cavities. Careful selection of deformation and heat treatment conditions during the processing steps can give a uniform and consistent microstructure in the tube, leading to improved deformability and lower manufacturing costs. Favorable microstructures were achieved in short test samples of RRR Nb tube, which may be particularly suitable for hydroforming into SRF cavity strings. The approach demonstrated could be applicable to microstructure engineering of other tube materials including tantalum, titanium, and zirconium.

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Purpose of the Phase I Project

The purpose of Phase I was to demonstrate the technical promise of a new method for fabricating polycrystalline Nb tube for SRF cavity applications that may be a cost effective alternative to methods currently used. The overarching technical objective was to refine and homogenize the microstructure in high RRR Nb tube to a level not easily achieved by conventional methods, and to demonstrate that this tubing has improved ductility for hydroforming. Specific technical objectives included:

- 1) Build fixtures to ECAE process tube geometries.
- 2) ECAE process polycrystalline high RRR Nb tubes.
- 3) Characterize the mechanical properties and microstructure of the ECAE processed Nb tube materials.

- 4) Identify processing routes (strain paths) which give promising microstructures for hydroforming into SRF cavity shapes.
- 5) Show that ECAE processed Nb tubing has good potential for hydroforming into an SRF cavity shape, and identify the technical benefits of ECAE tube processing.

Results from the Phase I work were to provide favorable answers to the following technical questions, to justify progression to a Phase II:

- 1) What are the microstructural characteristics (grain size, texture and microstructural uniformity) of Nb tube processed by ECAE?
- 2) What are the mechanical property differences between SPD processed Nb tube and commercially available Nb tube?
- 3) Does ECAE processed Nb tube have mechanical properties favorable for hydroforming into an SRF cavity?

Research Carried Out

Experiments were carried out primarily with high RRR Nb tube having nominal dimensions of 39 mm OD and 2.8 mm wall thickness. The tubes were processed by room temperature multipass-ECAE at Shear Form, Inc. (SFI) by the Principal Investigator (Robert Barber). ECAE tooling and an associated 380 ton press appropriate for processing Nb was used. Samples of ECAE processed Nb tube were sent to TEES and MSU for, mechanical property, electron microscopy, and texture characterizations. Post mortem analysis and property evaluations to better understand the microstructure – deformation characteristics of ECAE processed Nb tubes were done at SFI.

Research Findings

Materials and Methods

The materials used for the Phase I project included seamless OFHC Cu tube (1.5” OD with a 0.125” wall thickness), RRR Nb sheet (10” x 10” x 2.8 mm), and RRR Nb 7” long tube with nominal outside diameter 2” and a tapering wall thickness (from about 3 to 4 mm). The RRR Nb sheet and spun RRR Nb tube were donated to the project by FNAL. The spun Nb tube was fabricated at FNAL from 10”x10”x2.8 mm RRR Nb sheet. The donated RRR Nb sheets had an FNAL discovered defect, which made them unsuitable for deep-draw forming into ebeam welded SRF cavities.

The RRR Nb tube was the primary study material. It was ECAE processed. The Nb tubes were incased in OFHC Cu and the composite workpiece (square Cu can, Nb tube, and Solid Cu core) extruded as a solid block at room temperature. Embedded tubes were processed via several multipass schedules for up to 8 passes (strain of 9.6).

Processed tubes were carefully cleaned and recrystallized in vacuum (better than $10E-5$) at the DOE Ames Lab following standard procedures for Nb. The Nb tubes were extracted from their Cu encapsulations and annealed bare for these heat treatments. The heat treatments were done at 750C and 1300C to determine the characteristics of recrystallization at these two widely spaced temperatures. The objective is to develop a uniform recrystallized fine grain size in multipass ECAE processed material.

Materials characterizations included visual examinations, metallography, microhardness measurements, tensile testing, and scanning electron microscopy (SEM) EBSD analysis. Vicker's microhardness measurements, tensile testing, and optical microscopy were done at TEES. The EBSD analyses were done at MSU.

The tensile testing was done on small specimens extracted from the various materials by electro discharge machining (EDM). The gage dimensions for these specimens were 1 mm x 3 mm x 13.5 mm. These specimens were ground with 1200 grit polishing paper and chemically polished prior to testing to remove any surface deformation. Strain was measured by a sample-attached extensometer. Optical metallography involved mounting the specimens in a Bakelite mold and rough polishing using SiC grit paper and final polishing using 0.05 μm colloidal silica solution. The etchant used for metallography consisted of a 1:1:3 solution of concentrated HF: HNO_3 : Lactic acid. Vickers microhardness was determined using a LECO microindenter; the load used and dwell time used for the analysis were 300gms and 13s respectively.

Microstructures

(1) As-received Materials

The microstructure of the as-received 2.8 mm thick RRR Nb sheet is shown in Figure 1. The average grain size in this sheet is $31 \pm 20 \mu\text{m}$; regions of grain size banding are evident. This material was subsequently cold-formed into a cylinder to fabricate a 1.5" outside diameter (OD) 10" long tube.

Figure 1. This is a through thickness optical micrograph of as-received 2.8 mm thick RRR Nb sheet. There is slight banding (region of smaller grains) in microstructure as can be seen in the upper half region of the micrograph.

Figure 2. This is a through thickness optical micrograph of RRR Nb tube: c) the parent metal (Pm) region, which has a similar grain to the parent sheet; note the edges of the micrograph show smaller and elongated grains, which indicate local high strain at the sheet surface.

(2) ECAE Processed and Recrystallized Nb Tube

Strain in the Pm region seems to be relatively uniform, although evidence of shear banding at the 100 micron scale is observed.

When multipass ECAE processed tube is recrystallized, grain refinement is evident. The recrystallized grain size is larger for higher temperature annealing and shows signs of abnormal grain growth for high temperature annealing.

Figure 3. Optical micrographs of a RRR Nb tube processed by ECAE route 2C: c) the parent metal (Pm) with a recrystallized grain size of $132 \pm 43 \mu\text{m}$.

As the number of ECAE passes and recrystallization heat treatments increase, grain refinement increases and microstructural uniformity improves. This is evident in Figs. 4 and 5.

After ECAE processing (two 4E campaigns) and two recrystallization heat treatments (1300C and 750C), the microstructure appears to be quite uniform (figures 7b and 7c) with average grain size of $87 \pm 8 \mu\text{m}$ in the Pm region.

Figure 4. Micrographs of various sections of a tube processed via route 4E and recrystallized at 750C: b) the Pm region after 4E and 750C heat treatment with an average grain size of $92 \pm 31 \mu\text{m}$.

Figure 5. Optical micrographs of a RRR Nb tube sample after eight passes of ECAE and recrystallization at 750C: a) a section of the tube showing the Pm region (A), and b) the Pm has uniform grain size ($87\pm 8\mu\text{m}$) with equiaxed grains.

Mechanical Properties

Hardness Measurements

Representative Vicker's microhardness values for all RRR Nb samples are presented in Table 1. From these results, the following observations are made:

- (a) The hardness of ECAE processed tube increases as the number of passes increases.

- (b) After 4 or 8 passes with 1 or 2 recrystallization heat treatments (respectively), the hardness values of the Pm before and after ECAE processing are virtually the same.

Table 1. Vicker's microhardness for all RRR Nb materials tested in Phase I.

Material	Vickers Microhardness HV₃₀₀ Parent
2.8 MM Sheet (As-received)	55 ± 3
As-worked	
1A	101 ± 5
2C	125 ± 11
4E	146 ± 10
4E+1300C+4E	141 ± 5
Recrystallized	
1A + 750C	60 ± 8
2C + 750C	73 ± 2
4E + 1300C	53 ± 2
4E+1300C + 4E + 750C	53 ± 2

Tensile Testing

A summary of the tensile properties is given in Table 2.

Table 2. Summary of tensile properties on RRR Nb as-received sheet and ECAE processed 1.5” outside diameter tube.

Condition	Orientation	Yield (0.2% Strain)	UTS	Ductility at UTS (%)	Strain hardening exponent(n)
		MPa			
As received sheet		74	167	27.8	0.28
As formed tube		74	156	26.7	0.32
ECAE processed and recrystallized (8E + 750°C)		80	177	20.1	0.23

Notable observations:

- (a) The stress-strain curves (and associated tensile properties) for the as-received sheet and tube parent metal (Pm) are similar. This is expected, and confirms that the mechanical properties of the as-received annealed sheet do not change much by forming the sheet into tube geometry for relatively large bending radii and associated small levels of plastic strain.

- (b) The ECAE plus recrystallization tube parent metal YS and UTS are above those of the as-received sheet, while the corresponding ductilities are lower. This behavior reflects a smaller grain size in the ECAE plus recrystallization tube. These results are expected.

Estimate of Technical Feasibility

The Phase I results present strong evidence for technical feasibility of a method with commercial potential for fabricating/processing RRR Nb tubes of sufficient size for hydroforming into 1.3 GHz SRF cavity strings. These conclusions are based on two key findings:

- (1) ECAE processing with intermediate recrystallization annealing of RRR Nb tube can effectively refine the microstructure to an average grain size of 10-20 microns or above, depending on the final level of annealing and associated grain growth.
- (2) Plastic strain levels above four for each multipass-ECAE campaign combined with three or more recrystallization cycles can produce repeatable microstructures from different starting microstructures in pure Nb, providing the chemistry in the starting materials is the same. This result presents a strong argument for using severe plastic deformation processing to refine the microstructure of RRR Nb because one can then produce products with consistent final microstructures – something that is highly sought in the precursor tubes to be deformed (deep drawn or hydroformed) into SRF cavity strings.

Bibliography

1. Zamiri, F. Pourboghrat, H. Jiang, T.R. Bieler, F. Barlat, J. Brem, C. Compton, T.L. Grimm, "On mechanical properties of the superconducting niobium", *Materials Science and Engineering A*, 435–436 (2006), 658–665.
2. C. Compton, T. Bieler, B. Simkin and S. Jadhav, "Measured Properties of High RRR Niobium", NSCL-RIA-1 Report, Materials and Mechanics, Michigan State University (2000).
3. H. Jiang, T.R. Bieler, C. Compton and T.L. Grimm, "Evaluation of Recrystallization Textures from Cold Rolling Textures with Reversed Rolling in High Purity Niobium", *TMS Letters*, in press, (2004).
4. C. H. Rode, "Large Superconducting Radio Frequency Construction Projects", *IEEE Transactions on Applied Superconductivity*, paper 5LA01 in press (2005).
5. H. Jiang, T.R. Bieler, C. Compton and T. L. Grimm, "Mechanical Properties, Microstructure, and texture of Electron Beam Butt Welds in High Purity Niobium", *Proceedings of the 2003 Particle Accelerator Conference* (12-19 May 2003, Portland Oregon), IEEE Publishing, pp. 1359-1361 (2003).

6. P. Kniesel, V. Palmieri, K. Saito, "Development of Seamless Niobium Cavities for Accelerator Application." Proceedings of the 1999 Particle Accelerator Conference p. 943 New York.
7. W. Singer, "Seamless/bonded niobium cavities", *Physica C*, 441, (2006), 89–94.
8. H. Padamsee, J. Knobloch, and T Hays, *RF Superconductivity for Accelerators*, John Wiley & sons, Inc (1998).
9. T.L. Grimm, et al, "New Directions in Superconducting RF Cavities for Accelerators", *IEEE Transactions on Applied Superconductivity*, paper 5LA02 in press (2005).
10. Personal communications with Peter Kneisel (12/03/04) of Jefferson Laboratory.
11. S. I Wright, G.T. Gray III, and A.D. Rollett, "Textural and Microstructural Gradient Effects and the Mechanical Behavior of Tantalum Plate," *Met. Mat. Trans.* 25A, pp 1025-1031 (1994)
12. G. R. Myneni, P. Kniesel, and T. Carneiro, "Mechanical Properties of Three Types of RRR Niobium," 11th International Conference on Ultra High Purity Base Metals, UHPM 2004, Dec 6-9 2004, Gaithersburg, MD.
13. Thomas R. Bieler, "Advances in Material Studies for SRF" SRF09, 14th International Conference on RF Superconductivity, Berlin, Dresden, September 20-25, 2009, TUOAAU03.
14. D. Baars, T. R. Bieler, K. T. Hartwig, H. Jiang, C. Compton and T. L. Grimm, "Processing strategies for niobium sheet used in advanced superconducting particle accelerator cavities", *JOM* 59(6), pp 50-55, (June 2007).
15. H.Jiang, D. Baars, A. Zamiri, C.Antonie, P.Bauer, T.R.Bieler, F. Pourboghra, C. Compton, and T.L. Grimm, "Mechanical properties of high RRR niobium with different texture", *IEEE Transactions on Applied Superconductivity* 17 (2), pp. 1291-1294, (2007).
16. D. Baars, H. Jiang, T. Bieler, C. Compton, P. Bauer, T. Grimm, "Crystal orientations near welds in high RRR Niobium with very large grains", *Applied Superconductor Meeting*, Seattle, August 2006, in press, *IEEE proceedings*.
17. W. Singer, "Progress with Large Grain Cavities & Seamless Cavities", SRF09, 14th International Conference on RF Superconductivity, Berlin, Dresden, September 20-25, 2009, THOAAU04.
18. H. Jiang, T.R. Bieler, C. Compton, T.L. Grimm, "Creep and Dimensional Stability of High Purity Niobium Electron Beam Welds" (12th International workshop on RF Superconductivity (SRF 2005)), *Physica C* 441 (2006), pp. 122-25.
19. Ultrafine Grained Materials II, Proceedings of a TMS Symposium held in Seattle in 2002, Y.T.Zhu, et al editors.
20. K.T. Hartwig, J. Wang, D.C. Baars, T.R. Bieler, S.N. Mathaudhu and R.E. Barber, "Microstructural refinement of Nb for SRF Cavities", accepted for publication in *IEEE Transactions of Applied Superconductivity*, 2007.
21. V.M. Segal, "Materials Processing by Simple Shear", *Mat. Sci. Engr.* A197, p157-164, (1995).
22. K.T. Hartwig, D.O. Bryant, S.N. Mathaudhu, R.E. Barber and J.T. Im, "Grain refinement of niobium by severe plastic deformation", *Advances in Cryogenic Engineering-Materials*, Vol 50b, pp.441-449, 2003.
23. S.N. Mathaudhu, S. Blum, R.E. Barber and K.T. Hartwig, "Severe Plastic Deformation of Bulk Nb for Nb₃Sn Superconductors", *IEEE Transactions on Applied Superconductivity*, Vol. 15, pp. 3438-3441, 2005.