GRAIN GROWTH IN NIOBIUM FOR SUPERCONDUCTING RADIO FREQUENCY CAVITIES

A Senior Scholars Thesis

by

Joshua A. Vernon

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2009

Major: Mechanical Engineering

GRAIN GROWTH IN NIOBIUM FOR SUPERCONDUCTING RADIO FREQUENCY CAVITIES

A Senior Scholars Thesis

by

Joshua A. Vernon

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

Approved by:

Research Advisor: K. T. Hartwig
Associate Dean for Undergraduate Research: Robert C. Webb

April 2009

Major: Mechanical Engineering

ABSTRACT

Grain Growth in Niobium for Superconducting Radio Frequency Cavities. (April 2009)

Joshua A. Vernon
Department of Mechanical Engineering
Texas A&M University

Research Advisor: Dr. K. T. Hartwig
Department of Mechanical Engineering

This project explores the grain growth characteristics and grain morphology of bulk niobium (Nb) processed by severe plastic deformation (SPD). This report deals with factors affecting grain growth and recrystallization: purity, temperature, and time. Several heavily cold worked samples of varying purities (99.9X% and 99.99X%) were heat treated at varying temperatures and times to reveal grain growth behavior. Results presented include optical micrographs and grain characterizations in terms of size and morphology. Preliminary results indicate a significant amount of grain size banding in the recrystallized microstructures in the RG niobium. However, the RRR did not have the same banded microstructure. This may be an effect of the processing route or a result of the grain growth behavior in Nb.

DEDICATION

This thesis is dedicated to my supporting wife and best friend, Melissa.

ACKNOWLEDGMENTS

First and foremost, I would like to thank Shreyas Balachandran for his gracious support. He has given an infinite value in time, knowledge, and understanding in materials processing and how to approach this experiment. When I reached a place where I did not know or understand the next step, he took the time to explain what needed to happen and what direction I should go to make the most progress.

I must also thank Dr. Hartwig, my faculty advisor, for allowing me the opportunity to use his facilities, trusting me when he had no reason to, and helping me during the writing process. His patience and willingness to offer this project places him above most other faculty. Dr. Hartwig's expertise as a writer has helped me throughout this thesis to make it as painless as possible. Without this, the experience would not be nearly as enjoyable.

I also thank Jim Sajewski who helped me through the polishing process. As I started polishing, he pointed out a much faster and more efficient way that ultimately saved me weeks of labor and several headaches without compromising quality. The samples polished with his method yielded beautiful micrographs and great results.

Last, but not least, my wife Melissa has supported me every way she could when I was not in the lab. When I came home frustrated and confused, she would listen intently, whether she understood or not.

NOMENCLATURE

ECAE	Equal Channel Angular Extrusion
ASTM	American Society for Testing and Materials

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE Page

LIST OF TABLES

CHAPTER I

INTRODUCTION

All metals exhibit different behaviors according to their natural structure, chemical composition, and physical properties. These behaviors may be altered to achieve desired results with mechanical processing, thermal processing, or a combination of the two. Niobium is a hypoallergenic, refractory, transition metal with several applications. This research focuses on how niobium grains in heavily worked material grow after the grain recrystallization stage. The ideal results should include heat treatment conditions for grains ranging from a few microns to 1 mm. This wide range will show the full effect of heat treatment for various times and different temperatures. Two different sample purities were tested to show how chemistry affects these heat treatment results.

Initial samples

The initial samples were sectioned from billets thermo-mechanically processed by equal channel angular extrusion (ECAE). Three slabs of ¼" thickness taken from the central portion of the processed bar were cut with a diamond saw into sixteen equal-area samples per slab. Each sample has marks showing the ECAE direction and a unique numeric tag. The ECAE direction is marked to be able to orient grain morphology and

---

This thesis follows the style of International Journal of Refractory Metals and Hard Materials.

texture with the extrusion direction. Unique numerics enable determination of grain size uniformity. Figure 1 shows the identification scheme. Here, the arrows indicate the extrusion direction, the first digit indicates the row, and the second digit indicates the column.

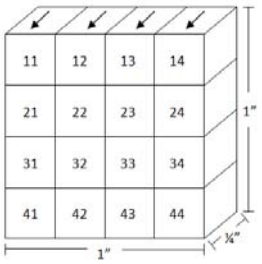

Figure 1.Sample identification schematic.

ECAE process

This is a process developed in the late 1970's to break up the microstructure of a material. It has been used to refine microstructures to the nano level. It has been done from 77-1500 K depending on the material and desired results [1]. Samples in this research were processed through four passes at room temperature by route A. The grains change as a sample experiences more passes through ECAE. Four route A passes would cause the microstructure to elongate along the shear plane of the process. Figure 2 shows how the grains change with route A ECAE processing.

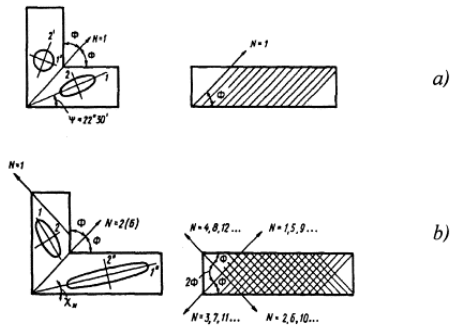

Figure 2. Simple shear during ECAE. (a) one cycle processing, (b) route 2A [2]

Route A means that the billet was not rotated between passes. Figure 3 shows different paths corresponding to different rotation schemes.

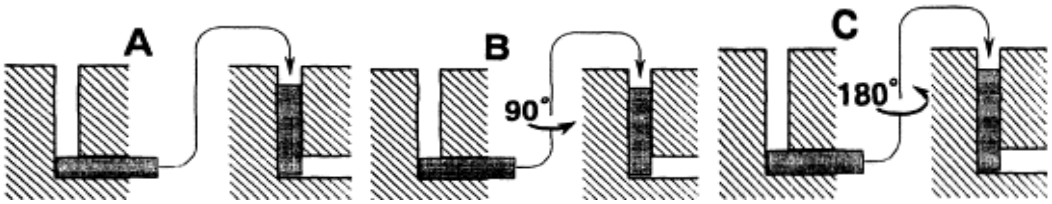

Figure 3. Versions of ECAE pressing for the first two passes. (a) route A, (b) route B, (c) route C [3].

Heat treating

Each heat treatment occurred in a vacuum chamber to reduce sample contamination through atmospheric oxidation. Since Niobium is a transition element, it has valence electrons available in more shells than just the outer layer. This causes several common oxidation states. Each oxidation state is a positively charged form, allowing different

ionic and partially ionic compounds [4]. These oxidation states cause low oxygen solubility which hinders grain growth.

Materials may be heat treated for several reasons. Depending on the time and temperature, heat treating can relieve internal residual stresses creating a soft, ductile metal. Annealing occurs in three stages: recovery, recrystallization, and grain growth.

Recovery

This is the first phase in a heat treatment cycle, which causes crystallographic change that occurs during annealing. It is often done to relieve stresses stored as internal strain by point defects and dislocations. Dislocation motion induced by ECAE can cause a reduction in dislocation occurrence and produces low strain energy dislocation configurations. The recovery process causes point defects to annihilate, dislocations to rearrange (but causes only slight decreases in dislocation density), and restores some physical properties to preworked states [5].

Recrystallization

Here, new strain free, equiaxed grains with low dislocation densities nucleate and grow. They typically nucleate at prior grain boundaries or in areas of high dislocation density

because the nucleation energy is much smaller there. This is a time and temperature dependent process. Ductility and tensile strength are inversely related to the percentage complete for this process. Figure 4 shows the general relationship between tensile strength, ductility, hardness, and original grain boundary morphology.

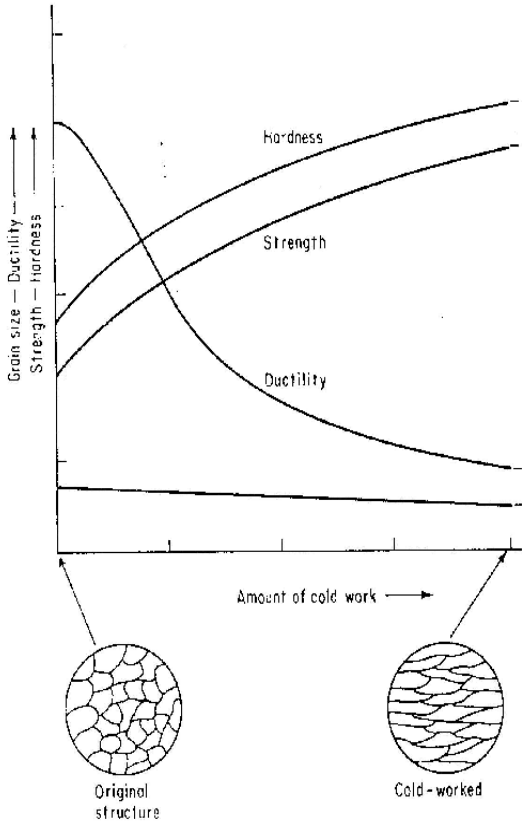

Figure 4. Ductility vs. strength as grain size changes [6].

Here, new grains will nucleate and start growing until the original strained material is depleted of excess strain energy from dislocations and new strain free grains develop. Recrystallization generally begins at about 30% of the material's melting temperature [5]. This is the starting point of the test matrix for this research.

Grain growth

Here, the new grains grow as the energy in grain boundaries is decreased. This is the heat treatment region of interest for this project. Purity plays a huge role here because grains grow more quickly at lower temperatures in higher purity materials. Some areas of the microstructure will have higher dislocation densities. This occurs because some areas have different starting textures. These regions with different textures deformed different during ECAE, and developed different final dislocation densities. Keep in mind that a "region" could have had its origin as one grain. The regions with different dislocation densities will recrystallize to different average grain sizes, and frow grains at different rates. This phenomenon can give rise to "banding" in recrystallized microstructures.

Sample chemistry

It is known that sample chemistry can affect the recrystallization temperature and grain growth kinetics. This may be the general chemistry or local chemistry within a specific region. Here, the general chemistry can change the activation energy and associated recrystallization temperatures for nucleation to begin. The temperature must break the activation barrier. The samples in this research will be of two separate chemistries, RG and RRR 300, to show how chemistry affects grain growth.

Applications

This research could help to better understand how to improve the formability of niobium for manufacturing. "The Fermi National Accelerator Laboratory is involved in the design and construction of superconducting particle accelerators. Many components require dense, non alloyed – high purity, high RRR, annealed Niobium. They are fabricated from plate and rod stock by machining as well as "deep drawing" or other metal-forming processes…" [7]. FermiLab requires Niobium that is at least 95% recrystallized, shows a uniform grain size of around 45 microns, and has equi-axed grains [7]. The grain size and geometry specifications are important in the machining and deep drawing process because a non-uniform structure may cause a non-uniform shape during forming.

CHAPTER II

METHODS

Standards are very important in experiments because they allow accurate result comparisons. All methods used in this experiment followed ASTM standards or were checked through redundant experimentation.

Sectioning

Billets were cut into sixteen samples using a diamond saw. The diamond saw is preferred over traditional cutting methods (e.g. band saw) because it allows only minimal surface deformation. It is important that the grains stay relatively unharmed during preparation of metallographic specimens. Deformed grains will affect material characteristics including grain count, size, and aspect ratio.

Each sample was identified using a unique number. Figure 1 shows the numbering scheme and sample dimensions. This allows others to reconstruct the billet after sectioning. This also helps sort the data to understand how heat treating and ECAE processing affects samples on the billet's edge. Edge effects may have an impact on the microstructure.

Heat treatments

Several heat treatments at different temperatures and time intervals will yield a data spread showing how niobium behaves. Since the chemistry is different between RRR 300 and RG, the heat treatment temperatures change to account for this influence. The heat treatments for RRR 300 are outlined in Table 1; Table 2 shows the RG treatments.

Table 1. RRR 300 Test Matrix.

RRR 300	580°C	630°C	680°C	730°C	780°C
10 minutes	312	713	113	714	514
60 minutes	512	411	412	311	213
180 minutes	811	111	212	513	112
600 minutes	314	712	614	214	611
1800 minutes	711	511	313	413	414

Table 2. RG Test Matrix.

RG	730°C	830°C	880°C	930°C	980°C
10 minutes	43	51	33	44	34
60 minutes	1	23	21	63	3
180 minutes	24	64	42	53	32
600 minutes	82	4	72	73	2
1800 minutes	31	71	52	41	61

In each test matrix, the sample number experiencing a specific heat treatment is written in the matrix. For example, sample 614 was heat treated at 650°C for three hours.

Furnace validation

It is important to have confidence in the heat treatments. That is to say that the entire sample experienced the same temperature throughout the experiment. This is a concern

when dealing with large samples. All samples in this experiment were small to minimize a size effect. Here, the temperatures in the furnace must be confirmed. A temperature profile of the furnace from end to end will show the variance along the furnace length. Figure 5 shows how the temperature changes as it is measured down the furnace length. Here, the target temperature was 500 degrees Celsius.

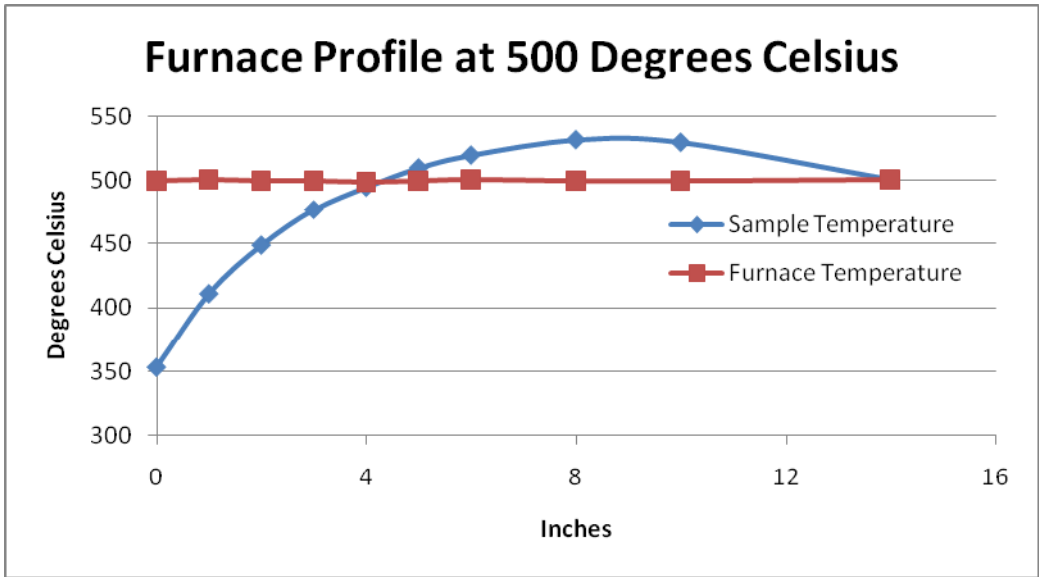

Figure 5. Furnace temperature profile with a set temperate of 750 degrees Celsius.

The furnace control has a thermocouple that measures the temperature indicated by the red line. We set a thermocouple in an extra niobium sample and measured the temperature indicated by the red line. After we received this data, our heat treatment temperatures were changed to reflect this offset.

Mounting

Samples were mounted according to ASTM E3-01 [8]. Here, four samples went into a pressurized cylinder with bakelite powder and placed under 4 kpsi pressure and heated up to about 135 degrees Celsius for 15 minutes until the bakelite hardened. Once the mounting hardened, the heater and mounted samples were removed from the cylinder. The sample ID numbers were etched into the backside of the bakelite.

Polishing

All polishing procedures followed ASTM E3-01 [8]. Once the samples were mounted, they were taken to a polishing wheel that resembles a pottery wheel. Each sample went through several polishing steps to achieve a surface containing scratches smaller than 0.05 microns. These scratches should not be seen at 40X magnification. Table 3 lists the pads and additives used in order to achieve such a finish.

Table 3. Polishing Pads and Additives.

Step	Pad	Additive	Load (lb./specimen)	Base Speed (rpm)/Direction	Time (min)
1	320 grit Carbimet®	water	6	150-250 Complementary	Until Plane
2	ULTRA-POL™ Cloth	9 m METADI diamond paste	6	150-200 Contra	20
3	TRIDENT™ Cloth	3 m METADI diamond paste	6	150-200 Contra	12
4	MICROCLOTH®	0.05 m MASTERMET colloidal silica	6	120-150 Contra	15

We used a Buehler Automet® automatic polisher to polish all samples. This machine has independent direction controls for the base that holds the pad and the head that holds the samples. This is where the base direction comes from. Complementary means the base and the head turn in the same direction and contra means the base and the head rotate in opposite direction. The speed only refers to the base speed since the head does not have a variable speed control.

Etching

After the mounted and polished samples were checked under a microscope for surface scratches, each sample went through an etching process that exposed the metal to chemical attack using the following recipe.

$$\text{Etchant} = 2 \text{ parts } HF + 1 \text{ part } C_3H_6O_3 + 2 \text{ parts } HNO_3$$

The chemical brew etches the material and makes the grains and grain boundaries visible under a low powered microscope. Figure 6 shows an example.

Figure 6. RG Nb annealed at 900 degrees Celsius for 90 minutes.

Analysis

Once the samples are mounted, polished, and etched, they are tested to determine their hardness and microstructureal characteristics. Hardness and average grain size are crucial for determining grain growth behavior. Other properties that can be determined are the grain aspect ratio, grain size distribution, and crystallographic texture.

Hardness

Hardness is directly related to material strength. Since tensile tests are destructive and difficult, hardness tests will suffice for this exercise. The hardness was determined according to the ASTM E 384-08 standard [9]. Here, each sample was placed under a microhardness indenter and tested using the Vickers hardness scale. This scale uses a square indenter. The machine indents the metal nominally with a 300-gram load and the

indention diagonals are measured. The machine then calculates the material hardness using these measurements. This process is repeated at least five times and the results are averaged.

Average grain size

Once the micrographs are taken, each picture is analyzed for the average grain size as set forth in ASTM E112-96 [10]. Here, a line is drawn across an image of the microstructure and grain boundary intersections with the line are counted. Then a mathematical ratio relating magnification to the picture size is calculated. The image grain size is determined by taking into account the magnification and the number of grain boundary intersections.

CHAPTER III

RESULTS

At lower temperatures, our results show how pure niobium recrystallizes. While it is interesting to see this phenomena occur, it is not our primary concern. We also see some varying grain size banding in all of the RG samples. This banding phenomenon became the focus of this research project.

Recrystallization

Figure 7 shows wide angle micrographs of each sample heat treated at 700 degrees Celsius for varying times. These micrographs show how the material recrystallizes as it is heat treated for longer time periods.

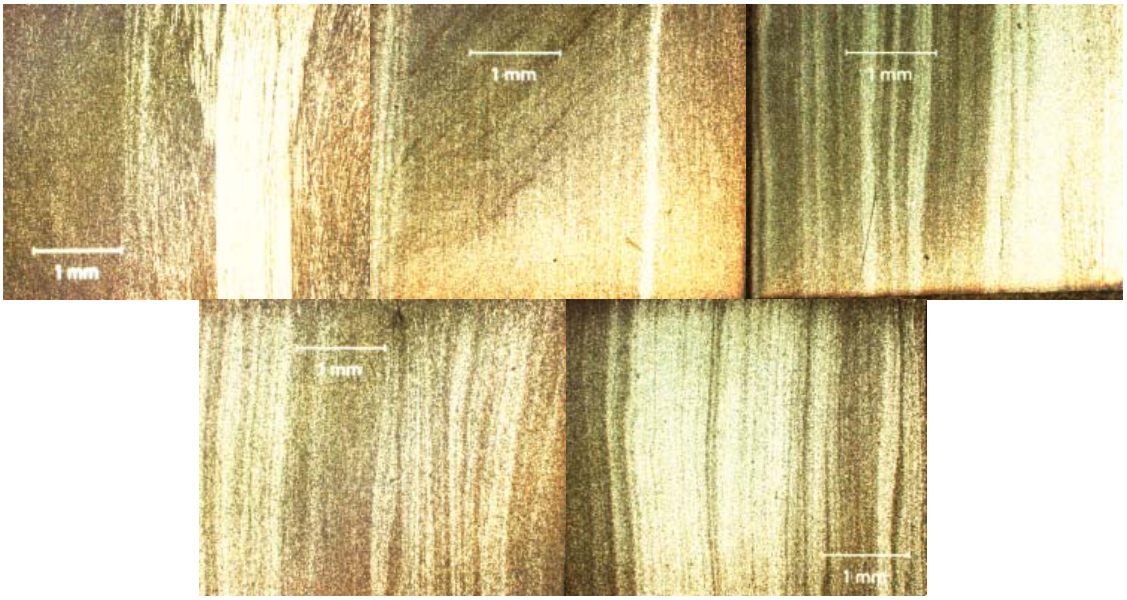

Figure 7. RG NB heat treatments at 700 degrees Celsius in varying times. (a) 10 minutes (b) 60 minutes (c) 180 minutes (d) 600 minutes (e) 1800 minutes.

Here, it is important to note that color does not always indicate recrystallization. The white region in figure 7a shows smeared grains from the polishing process. Figure 7a shows a closer magnification of this region and figure 8b shows the rest of the material. It is apparent at this magnification that no recrystallization has occurred.

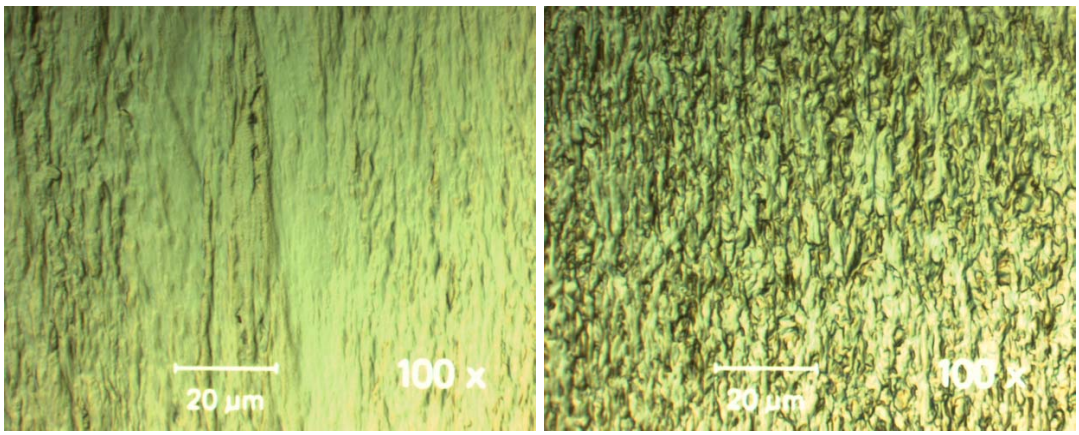

Figure 8. RG Nb heat treated at 700 degrees Celsius for 10 minutes. (a) smeared grains (b) unrecrystallized grains.

This material would be considered 20 percent recrystallized. From here, the material will recrystallize in a logarithmic fashion. Figure 9 shows a graph of percent recrystallization vs. time for copper to illustrate general recrystallization behavior.

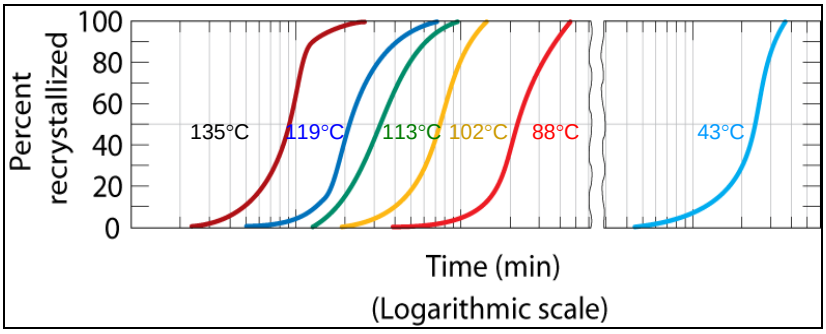

Figure 9. Recrystallization graph of copper [11].

Notice here that as the temperature decreases, the time to recrystallize increases. Our samples also trade off time and temperature during recrystallization. Figure 10 shows some micrographs of other samples heat treated at 700 degrees Celsius for other times. The percent recrystallization increases as grains appear over more surface with increasing time.

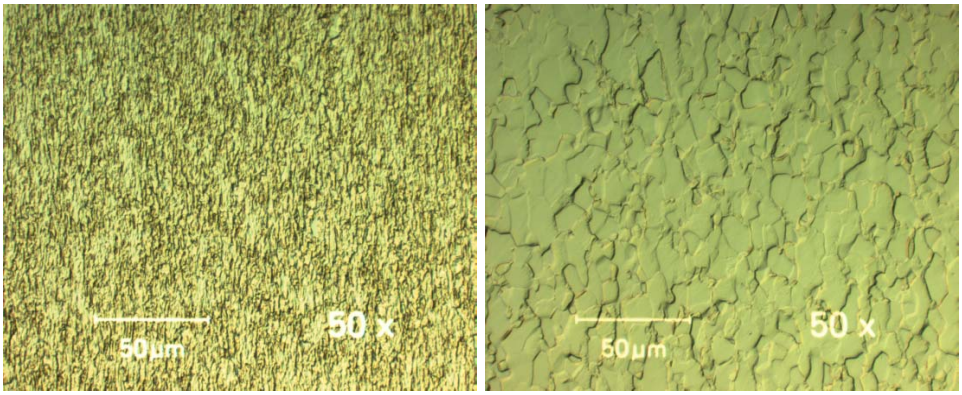

Figure 10. RG Nb heat treated at 700 degrees Celsius for 60 minutes. (a) unrecrystallized region (b) recrystallized region.

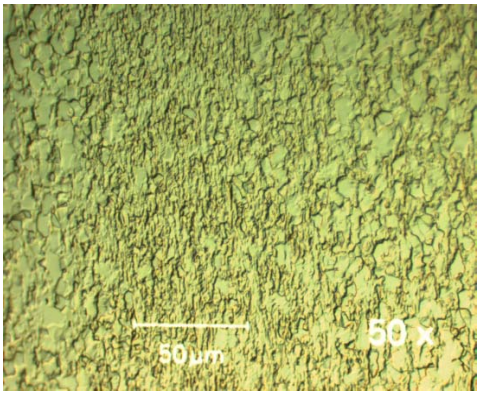

Figure 11. RG Nb heat treated at 700 degrees Celsius for 180 minutes.

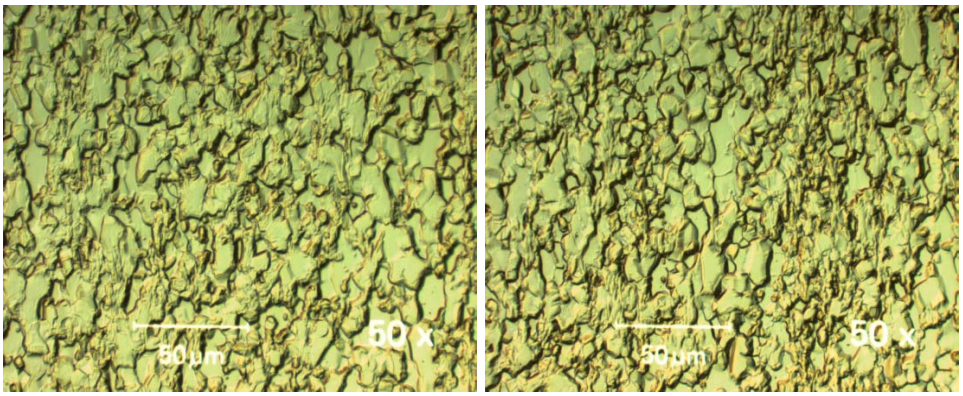

Figure 12. RG Nb heat treated at 700 degrees Celsius for 600 minutes.

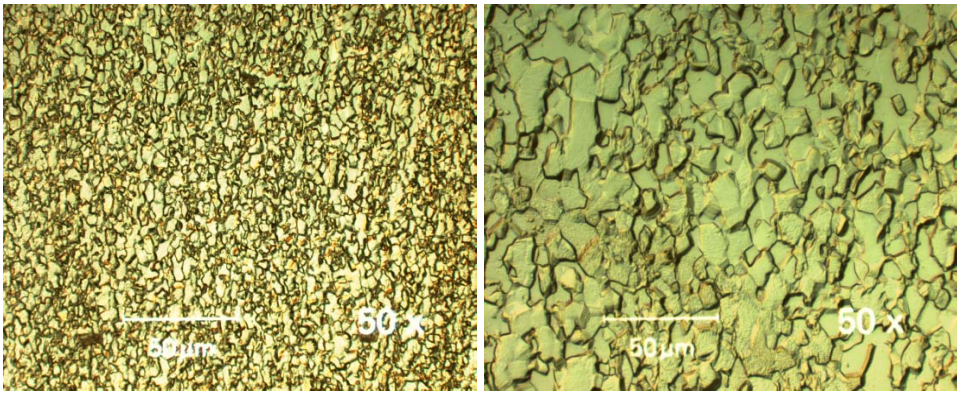

Figure 13. RG Nb heat treated at 700 degrees Celsius for 1800 minutes.

Grain growth

The other RG samples also showed grain growth beyond the recrystallization phase. While this growth occurred in deformation bands, the banding effect diminishes with increasing temperature. Here, samples heat treated at lower temperatures show bands with small differences in grain size. This structure is dominated by bands with two grain sizes: small and large. Figures 14 and 15 show how the grain sizes vary in these bands.

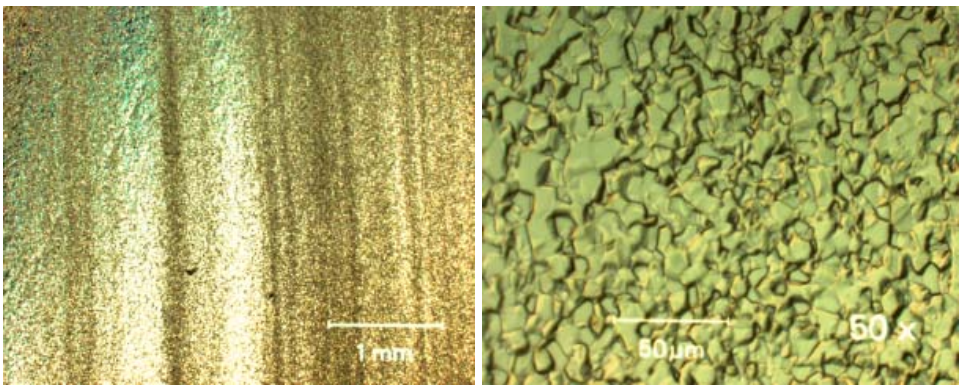

Figure 14. RG Nb heat treated at 900 degrees Celsius showing different grain size deformation bands. (a) at 2.5x magnification (b) at 50x magnification

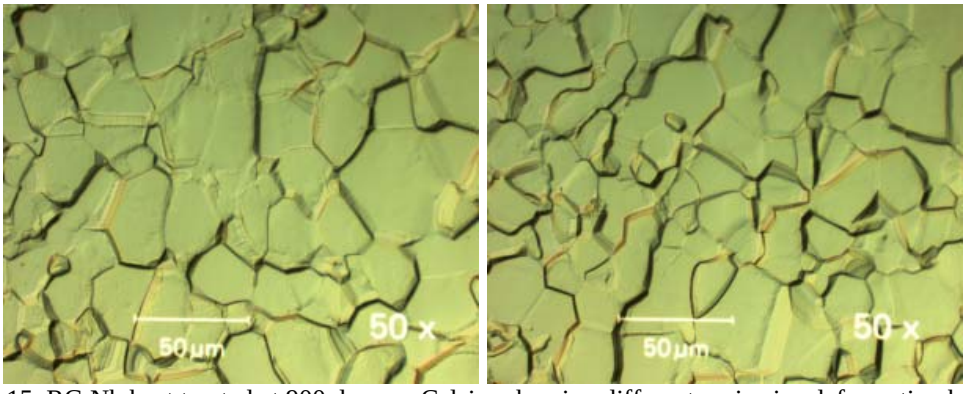

Figure 15. RG Nb heat treated at 900 degrees Celsius showing different grain size deformation bands at 50x magnification.

As time increases, the large grain bands outgrow the small grain bands. While the small grain bands show some growth, growth tapers off over long time periods. Figure 16 shows how the grains grow with respect to time.

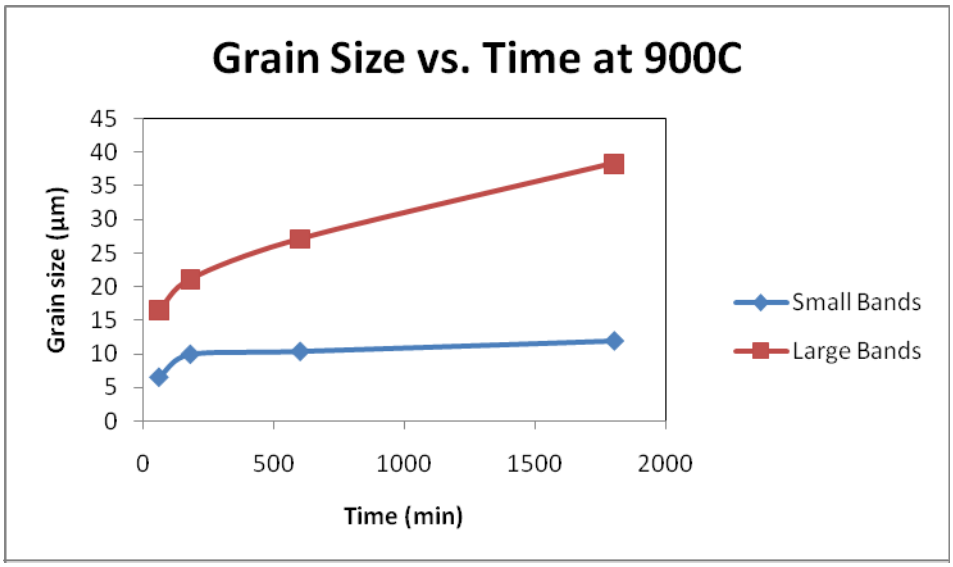

Figure 16. Grain growth in RG Nb heat treated at 900 degrees Celsius for times up to 1800 minutes.

While grains grow at a single temperature with increasing time, they also grow at a single time with increasing temperature. Here, the grains actually grow faster than with increasing time. Figure 17 shows how grains grow with increasing temperature at a constant time.

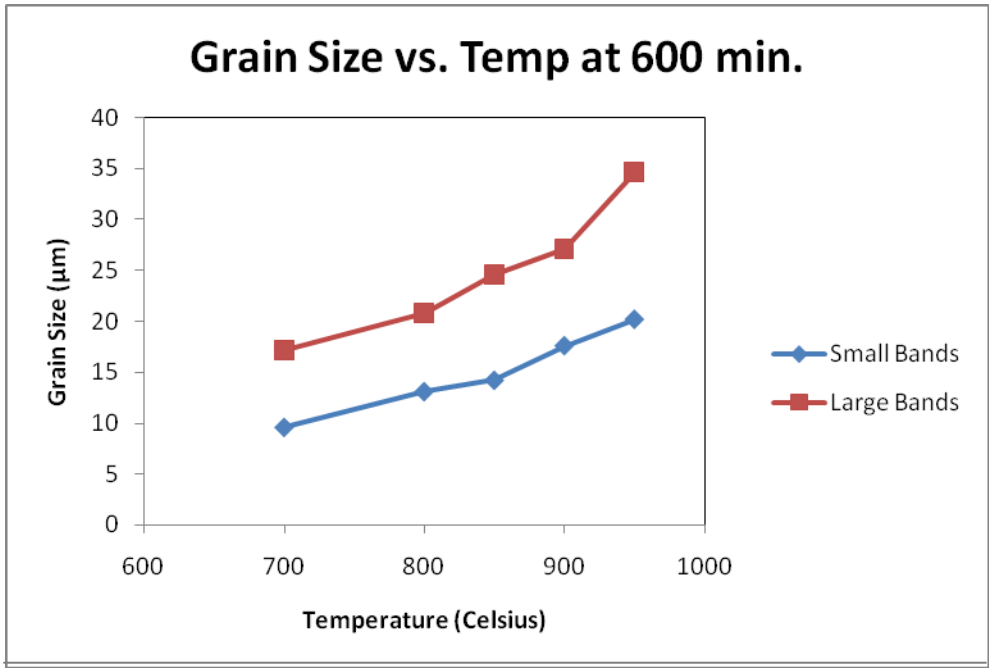

Figure 17. Grain growth in RG Nb heat treated at 600 minutes for varying temperatures.

Here, it is obvious that the grains grew equally in each band size until the end of the graph. This may indicate that we have plotted the very bottom of the grain growth region. As more data is collected at higher temperatures, this graph may diverge with higher temperatures in an exponential pattern.

RRR

The RRR test matrix is not complete, but we did finish some key heat treatments which indicate certain results across the entire matrix. There was no deformation banding in any of the RRR samples and we mostly saw uniform grain growth at all tested times and temperatures. We also saw 100 percent recrystallization at 550 degrees Celsius after 30 hours and 100 percent recrystallization at 750 degrees Celsius after 10 minutes. This

indicates that our test times and temperatures are valid for the bottom of the grain growth region.

CHAPTER IV

SUMMARY AND CONCLUSIONS

During the ECAE process, the work piece experiences high, uniform strain. During this, individual grains subdivide into crystals with different orientations. These diverging crystal orientations then deform by different slip systems, which leads to deformation banding. Since this type of inhomogeneity is very visible with an optical microscope, it has been noted since the late 1930's. Deformation twinning, which may occur in bcc metals deformed at low temperatures with high strain rates, is one such deformation mode that may influence banding. These bands will inevitably form when deforming polycrystals. The banding details change with the deformation process. For example, the same material would produce two different results if one sample was deformed by rolling and the other by ECAE [12].

Since each sample experiences deformation banding from the ECAE process before the heat treatment phase, it is understandable that the grains would also grow in this banding formation. The resulting grain size graphs show that this banding tendency continues throughout the each phase of the heat treating process. The larger grains recover first, recrystallize faster, and grow larger, until they squeeze out smaller grains because of surface energy differences.

In addition to noting that deformation bands are present in all RG samples, it is also important to note that as the heat treatment temperature increases, these bands diminish. This means that while the difference in grain size increase, each large grain band consists of more area. This is particularly evident in the sample treated at 850 degrees Celsius for 10hours. Figure 18 shows this sample.

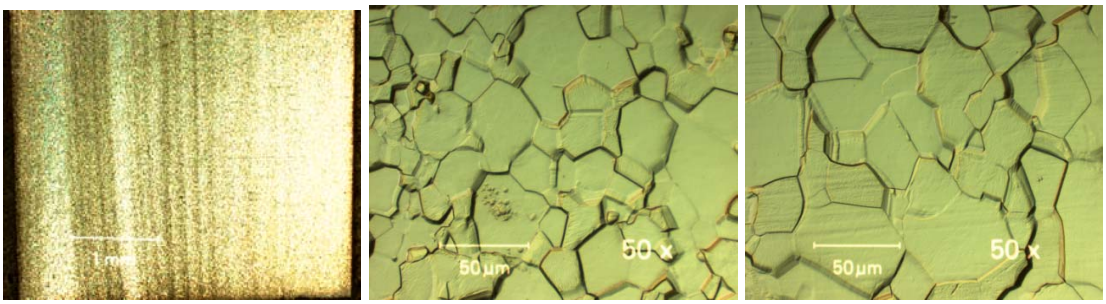

Figure 18. RG Nb heat treated at 850 degrees Celsius for 10 hours in varying magnifications. (a) magnified at 2.5x (b) top right corner magnified at 50x (c) bottom right corner magnified at 50x

Here, nearly the entire right side of the sample shows a relatively uniform large grain size. From the right side, there is very little variance in grain size as evident from figure 17b and c. The left side shows light deformation banding. Figure 19a and b show a few micrographs of how the grains vary in size.

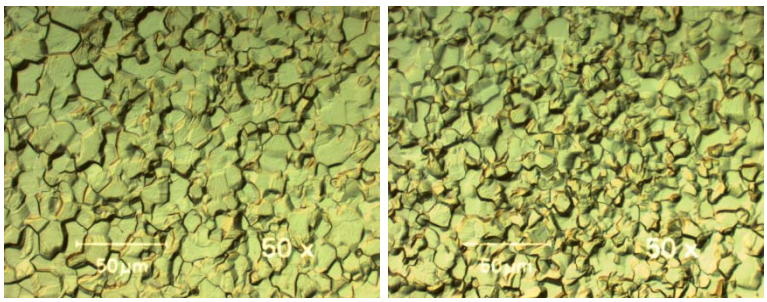

Figure 19. RG Nb heat treated at 850 degrees Celsius for 10 hours. (a) upper left corner magnified at 50x (b) lower left corner magnified at 50x.

Thus, this project yields several conclusions. First, different crystal orientations cause grain size banding within the microstructure. These crystal orientations are a result of the ECAE processing and do not change orientation during the heat treatment process. Second, banding diminishes as the heat treatment temperature increases. This explains why industry heat treats pure niobium at extremely high temperatures (1200 degrees Celsius for one hour in a material cold worked over 50 percent) [13]. Finally, large grains outgrow small grains because their growth requires less surface energy.

REFERENCES

1. The ECAE Group's Home Page. http://www1.mengr.tamu.edu/ecae/INDEX.HTML. Accessed 21 November 2008.
2. Segal, V.M., Reznikov V.I., Kopylov V.I., Pavlik D.A., Malyshev V.F. *Processes of Plastic Transformation of Metals.* Navuka i Teknika, Minsk, Belarus 1984; 295.
3. Iwahashi Y., Horita Z., Nemoto M., Langdon T.G. *Acta Materialia* 1998;46; 1589.
4. Transition Metals – Properties of Element Groups. http://chemistry.about.com/od/elementgroups/a/transitionmetal.htm. Accessed 13 November 2008.
5. Callister, W.D. Jr. *Materials Science and Engineering.* Sixth Edition, Wiley & Sons, Inc., Hoboken, NJ, 2002.
6. Farmingdale State College. Cold Work (class notes from MET 205). http://info.lu.farmingdale.edu/depts/met/met205/coldwork.jpg. Accessed 8 December 2008.
7. Antoine and Bauer. Technical Specifications for High RRR Grade Niobium Sheet and Rod for use in Superconducting Cavities. Fermi National Accelerator Laboratory. Batavia, IL. 4 April 2006.

8. ASTM Standard E 3, 2001 (2007), Standard Guide for Preparation of Metallographic Specimens. ASTM International, West Conshohocken, PA, www.astm.org.
9. ASTM Standard E 384, 2008, Standard Test Method for Microindentation Hardness of Materials. ASTM International, West Conshohocken, PA, www.astm.org.
10. ASTM Standard E 112, 1996 (2004)e2, Standard Test Methods for Determining Average Grain Size. ASTM International, West Conshohocken, PA, www.astm.org.
11. Nottingham. Heat Treating Non-Ferrous Metals. University of Michigan, Flint, MI, www.umflint.edu
12. Humphreys, F.J., Hatherly M. *Recrystallization and Related Annealing Phenomena* Elsevier, Boston, 2002; 26-48
13. REMBAR Niobium Technical Info. http://www.rembar.com/niobium.htm Accessed 8 April, 2009.

CONTACT INFORMATION

Name:	Joshua A. Vernon
Professional Address:	c/o Dr. K.T. Hartwig Department of Mechanical Engineering MS 3123 Texas A&M University College Station, TX 77843
Email Address:	cagen08@gmail.com
Education:	B.S., Mechanical Engineering, Texas A&M University, December 2009 Undergraduate Research Scholar Corps of Cadets