PROJECT DESCRIPTION
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Relationships between deformation and microstructure evolution and minimizing surface roughness after BCP processing in RRR Nb cavities

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Recent progress in developing radio frequency superconducting cavities has focused on a variety of processing paths to obtain a defect free ultra smooth surface that enables extremely high field gradients to be maintained without quenching the field. A number of processing variables have been proposed as being important for attaining a defect free surface necessary for achieving high field gradients. These are 1) by elimination of grain boundaries by using single crystals to fabricate cavities, 2) control of the distribution of grain orientations to prevent differential etch rates, and 3) a fine grain size to minimized surface topography during forming. To enhance superconductivity in cavity surfaces, vacuum anneals have been proposed as a method to reduce the oxygen concentration on the surface as a final enhancement for any of these forming paths.

To date, preliminary efforts to examine these effects have brought modest understanding about fundamental relationships between microstructure evolution and its effects on the cleaning and etching processes used to develop optimal surface functionality of the cavity. In part, this has been due to the need to develop infrastructural methods to clean and maintain cleanliness of the interior cavity surfaces, such as the buffered chemical polish and electropolishing methods. Therefore it is important to develop understanding of how microstructure and microstructural evolution
during processing affects the ability to achieve a polished surface with minimal surface roughness.

Therefore we propose to examine issues that have arisen from preliminary studies of the relationship between microstructure and surface properties more systematically. The preliminary studies have been based on the following strategies; their motivating hypotheses and open questions are indicated below.

**Background**

The issue of surface roughness on the interior of cavities has been examined to determine whether surface roughness on a small scale may account for differences in performance between cavities with different processing histories. For example, a buffered chemical polish causes the surface roughness of a rolled sheet to increase, as illustrated in Figure 1. Recent surface roughness measurements have been correlated with differential etch rates on grains with different orientations, [Lee]. For example, Figure 2 shows a ledge at a high angle boundary on a buffered chemical polished surface. Furthermore, magnetic flux penetration has been shown to be enhanced by grain boundaries, particularly on etched surfaces [Polyanskii].

In polycrystalline high RRR sheet processed by Tokyo Denkai, the distribution of crystal orientations on the surface differs from the center as illustrated in Figure 3(left),

**Figure 1** Surface roughness measures using a Veeco system. After a buffered chemical polish, the roughness becomes worse, rather than better.

**Figure 2** Effect of etching on developing grain boundary steps at grain boundaries (a) with high angle boundary misorientations (b), and trapped magnetic flux penetration (c) [Lee, Larbalestier, Gurevich, Squitieri, Starch, Polyanskii].
while in contrast, sheet metal processed by Teledyne Wah Chang in Figure 3(right) shows a more uniform distribution of crystal orientations on the surface and throughout the thickness. Blue orientations have an orientation close to $<111> \parallel \text{ND}$, and red orientations are close to $<001>\parallel \text{ND}$. The distribution of crystal orientations (aka texture) are often presented as pole figures. The $\{001\}$ pole figures exhibit the $<111> \parallel \text{ND}$ as a ring tilted $54^\circ$ from the center, which is known as the “$\gamma$ fiber”. Given that surface energy is a strong function of crystal orientation, this implies that processing history should have a significant impact on etching of a surface. However, little is known about how the surface texture affects surface-etch characteristics.

Rolling of BCC metals such as niobium tends to develop an increasing fraction of grain orientations with $<111>$ parallel to the surface normal with increasing reduction. Figure 5 shows how this changes between 70, 80, and 90% reduction of a thick plate to form a thin sheet. This laboratory experiment generated crystallographic textures more similar to the Wah-Chang specimen than the Tokyo Denkai specimen. The intensity of the $\gamma$ fiber quantifies the fraction of crystal orientations with this desired orientation increases in a complex way with processing history, becoming strong only with large amounts of reduction, as indicated by the $\gamma$ fiber intensity plot in Figure 4.

Assuming that a good surface etch can be achieved, surface oxidation will occur at different rates, depending upon the crystal orientation. Figure 5 shows a region near an e-beam weld that had not completely cooled before exposure to air. The grain structure is
clearly apparent as a few grains oxidized much more aggressively than others, evident as a darker brown color. Such grains are hypothesized as being those with lower probability orientations, such as \( <001> \parallel ND \) orientations (red in Figure 3). Figure 6 shows results from an XPS measurement of surface concentration of elements with respect to depth. The surface Nb concentration increases from 10 to 60% within a couple nm, while O drops correspondingly. A small amount of F from the HF in the etch (as well as Zn and Na impurities) was embedded in the surface oxide. Preparations are under way to measure changes in surface concentration after in-situ vacuum heating to temperatures between 150-250\(^\circ\)C to determine how oxygen transport into the Nb could alter the surface oxide.

**Research Plan**

Three strategies for improving the surface finish of niobium sheet are proposed, first to examine how process variables such as crystal orientation and welding affect the “single crystal” material that has recently been shown to provide a cost effective alternative to rolled material. Second, the effects of rolling variables on surface texture and dislocation density will be examined so that optimal approaches to rolling and recrystallization may be determined based upon fundamentals of metal physics. Third, it is possible to further reduce the grain size and improve rolling uniformity using equal channel angle extrusion to pre-condition billets before rolling. This approach provides a way to reduce the heterogeneity in the microstructure, which may improve etching characteristics.

1. **Removing grain boundaries entirely by using single crystal sheets to form cavities.**

   The rationale for this novel approach [Ganapati] is that grain boundaries are problematic because they are the origin of heterogeneous strain and heterogeneous oxidation, as air was let back into the E-beam weld chamber, showing that some grain orientations oxidize faster than others.
surface energies in the first place. It is important to determine how robust this approach will be, by evaluating effects of a number of variables on etching behavior. For example, sheets of material cut from an ingot by EDM have initial surface roughness due to the recast layer, but if etching occurs at a constant rate on all surfaces, it may require much material removal before geometric surface undulations can be smoothed out. Therefore it is important to determine how much material must be removed to attain a sufficiently smooth surface.

There is a related concern about the effect of crystal orientation on the ability to achieve a smooth surface. If the surface grain orientation has a naturally high energy, then there may be 2-4 low energy planes with surface normal directions close to the specimen normal direction, such that the total surface energy may be minimized by revealing these multiple low energy surfaces simultaneously – leading to a rougher surface (see schematic illustration in Figure 7). This would imply that there would be some crystal orientations that would etch toward perfectly smooth surfaces and others that would etch toward a bumpy surface. Consequently it will be important to identify which crystal surfaces have lowest energy in the chemical polishing environment. Thus a series of surface roughness measurements following etching on samples with different crystal orientations will indicate which crystal orientations should be avoided, as well as which orientations should be sought when developing technology to produce single crystal ingots. Preliminary attempts to reproduce the mirror finish reported by Ganapati indicated that the quality of the finish depended on the etch time, but it is not clear whether the crystal orientation was also affecting the ability to obtain a mirror finish.

Related to the issue of crystal orientation is the rate of oxidation, as illustrated in Figure 6. Given that a low temperature anneal in vacuo can cause surface oxygen to diffuse inward, the surface superconducting properties may be improved. However, it is important to determine how the effect of crystal orientation may affect the time and temperature needed to obtain optimal oxygen diffusion away from the surface. Therefore XPS studies with in-situ heating with different single crystal orientations will provide experimental data needed to identify optimal conditions.
A second concern about use of single crystals to form cavity halves is related to the strain required to cause recrystallization, which would cause multiple grain orientations and hence, differential etch rates. Because welds are located at regions with large strains in the cavity preforms, temperatures will surely reach levels where recrystallization is likely, if the dislocation density accumulation is sufficiently large. For example, in pure aluminum polycrystals, a tensile strain of 5% is sufficient to generate 100 recrystallized grains per cm$^2$ in a 2 hour anneal at 350°C (Anderson and Mehl, 1945). There is a rich literature that has examined recrystallization mechanisms in single crystals. This literature shows that the amount of strain required to nucleate recrystallization varies with the crystal orientation, the amount of strain, and the heating rate. Consequently, a review of this literature is desirable to identify strategic experiments that will provide fundamental ways to predict how much deformation can be tolerated, and what heating rates must be used to prevent recrystallization (that is, to stimulate recovery so that recrystallization is precluded). With such criteria, it would be possible to predict whether welds will cause recrystallization in a cavity with a given crystal orientation.

Some preliminary results from texture measurements of single crystals with two different initial orientations showed no obvious recrystallization after an e-beam weld was put on one end of the deformed strip. In one severely strained specimen with the bending axis parallel to the crystal $<111>$ direction and specimen normal direction, the $<111> \parallel$ ND orientation was maintained with no apparent different orientations, though the detailed orientation of the unit cell about the rotation axis changed with location according to the bent shape. In another specimen with a small strain without $<111> \parallel$ bending axis, no new orientations were observed. This suggests that dislocations in true single crystals are able to enter and leave on opposite sides of the material without accumulating sufficient dislocation density to generate a recrystallization nucleus in the short time associated with a weld. However, future experiments will examine if this is sensitive to crystal orientation, or if grain boundaries will entrap a sufficient dislocation density to stimulation recrystallization.

Also, Bieler will be collaborating with Raabe et al. at the Max Planck Institute für Eisen Forschung (MPIE) in an effort to characterize strain gradients near boundaries using samples consisting of bi-, tri-, and multi-crystal RRR Nb obtained from ingots during early 2006. Thus, once these specimens are characterized for local strain effects, recrystallization studies can be conducted as well.

2. **Altering deformation history to minimize the heterogeneous distribution of crystal orientations on the surface.**

The rationale for this approach is that processing material to have grains on the surface with nearly the same crystal direction normal to the surface could reduce the differential surface energy in adjacent crystals, and hence minimize differential etch rates. Preliminary studies have suggested that strategic processing paths may be possible to reduce or eliminate heterogeneous surface orientations, such as those illustrated in the sheet Nb microstructures and textures in Figure 3. For example, large reductions followed by recrystallization can give different results as illustrated by the Tokyo-Denkai specimen and a Teledyne Wah-Chang rolled specimen. Preliminary studies have shown
no dramatic difference in statistical measures of surface roughness with differences in reduction, but the overall surface topography differs. One possible reason for this lack of improvement in surface roughness is due to insufficient etching time, the effects of which need further investigation.

However, even if the crystals on the surface have nearly the same orientation, they may still etch differently if the dislocation density is not homogeneous, as niobium is known to be subject to shear banding [Raabe]. This implies that characterization of the variation in dislocation density in addition to crystal orientations need to be quantified, as well as the effect of annealing on dislocation density, to identify relationships between microstructure and substructure on etching rates. Semi-quantitative measures of defect density can be obtained from orientation imaging microscopy, but TEM measurements on strategic specimens should provide more convincing measurements of dislocation density effects.

Second, the preliminary laboratory rolling studies in Figure 3 and 4 above were made on one specimen, using a tapered slab rolling procedure to achieve a gradient in rolling reduction. However, the strain path in the tapered slab is different from more conventional rolling reduction. Thus it is important to determine if the nearly homogeneous texture on the surface can be reproduced using a more conventional rolling schedule, and to determine if varying the reduction per pass (a rolling process variable) will alter the nature of the surface texture significantly.

3. **Processing material to obtain a fine, recrystallized grain size.**

The rationale for this approach is that when the sheet metal is deformed to make cavity halves, a finer grain size will cause more homogeneity in the deformation (a smaller mean free path for dislocation travel, and hence, less likelihood of developing shear bands), and thus a more homogeneous distribution of stored strain (defect) energy. When chemically polished, material should be more evenly removed. Thus, it is not clear if the currently available 20-50 micron grain size material represents the smallest practical grain size that is achievable.

A phase I SBIR study is under way to examine how equal channel angle extrusion can be used to refine the grain size in a billet in order to obtain smaller and more uniform grain sizes, so that subsequent rolling may occur more homogeneously than has been presently achieved (note the variation in grain size and texture in the Teledyne Wah-Chang material in Figure 3). Equal Channel Angle Extrusion has been used to obtain a nano-scale recrystallized grain sizes when annealed strategically. Bieler is collaborating with K. Hartwig to examine the feasibility of producing smaller grain size material than is currently available, and it would make sense to include etching studies (with surface roughness measurements) as part of the planned (Phase I SBIR) microstructure characterization in this developing program.

**Broad Impact**

It is well known that the performance of superconducting cavities can be enhanced by having an excellent surface finish. While cleaning and etching methods have been developed in a number of labs to enable super-clean surfaces to be obtained, the influence of the microstructure and forming history on the surface finish is not well understood.
Developing understanding of how microstructural characteristics affect cavity performance will allow specifications for processing of cavities to be specified. The research described in this proposal will establish cause and effect relationships between processing history and cavity performance, which will ultimately lead to repeatable production of high performance high RRR Nb cavities.

Facilities, Equipment, and Other Resources

Microstructural characterization that includes the effects of crystal orientations is accomplished with orientation imaging microscopy. We have a TexSEM Laboratories version 3.1 software installed on our Camscan 44FE microscope, with associated hardware, that is able to measure and index electron backscatter patterns about 20 pixels per second. In addition to this facility, we have two Scintag XDS 2000 x-ray diffractometers, one for normal diffraction and the other with a dedicated pole figure goniometer system. Texture measurements using x-rays is necessary when the dislocation density is too high, so as-rolled specimens are most effectively analyzed with x-rays. Within the Composite Materials and Structures Center (in the same building), there are a number of facilities such as nano-indentation, Atomic Force Microscopy, XPS and Auger Electron Spectroscopy systems. While not a focus of this proposal, Instron Universal Testing Machine and an ATS 2710 Creep (Stress-relaxation) machines are available, and have been used on related studies. We have access to a Veeco optical surface roughness measurement tool in the GM Research Laboratories in Warren, MI.

Research Time Line

The proposed work would be accomplished over two years, and it is leveraged with related research activities on other funded research programs, such as the SBIR for equal channel angle extrusion and Bieler’s sabbatical at MPIE. The research activities described above are planned as follows:

Activity and quarter: 1 2 3 4 5 6 7 8
1. Single Crystal:
effect of EDM surface roughness on etch
   effect of x1 orientation on etch rate
   effect of x1 orientation on O absorption/diffusion
   effect of grain boundaries on Rx
   effect of weld on Rx
   dislocation accumulation in Sx1
Analysis and reporting

2. Rolling Deformation History
Rolling with different reductions/pass
Measurement of texture gradients
Characterization of dislocation density
TEM study of recovery/Rx mechanisms
Analysis and reporting
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3. Equal Channel Angle Extrusion
Measurement of texture in ECAE billets --SBIR---
Measurement of texture in rolled billets ---SBIR----
Seek optimal Rx conditions ---------
Etching studies --------------
Analysis and reporting --SBIR--- -------

Budget Justification

Three-year budget in then-year k$

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References

Myneni, G., “Physical and mechanical properties of single and large crystal high-RRR niobium”, Proc of the 12th International workshop on RF Superconductivity, Ithaca NY (2005)


A.A. Polyanskii, “Magneto-Optical Imaging of Nb Samples for RF Cavity Applications”, Collaboration Meeting on SRF Material Research, May 4th, 2005, FNAL