CHARACTERIZATION OF NIOBIUM FILMS AND A BULK NIOBIUM SAMPLE WITH RRR, SIMS AND A SQUID MAGNETOMETER

L.N.Hand, Physics Dept., Cornell University, Ithaca, NY, 14853 USA#

J.P.Craig and J.A.Thompson, CCMR REU Program, Cornell University, Ithaca, NY, 14853 USA*

W.R.Frisken, Dept. of Physics and Astronomy, York University,Toronto,Ontario, M3J1P3 Canada

Abstract

A variety of tests were performed on bulk niobium and niobium films produced by DC magnetron sputtering in argon on both copper and sapphire substrates. The films on sapphire were epitaxial. Clear differences emerged between these different samples, and criteria for improved niobium film-based cavities were established. These are listed at the end of this report.

INTRODUCTION

Three types of tests were performed on niobium films and on a sample of bulk niobium supplied by DESY[1] which had a nominal RRR of 282. The RRR of the epitaxial films was measured using a four point van der Pauw technique with gold contacts sputtered at the corners of the film. RRR values ranged from 4.1 to 65.3. The niobium film on a copper substrate was produced at CERN[2,3]. It was measured there to have a RRR of 11.5+/-0.1.

X-ray measurements were taken to learn the degree of orientation of the films, and, for the Cornell films, to verify that they were epitaxial. This was done at the GADDS facility of CCMR[4]. The Cornell films consist of 110 planes parallel to the substrate, without grain boundaries. Film thicknesses were determined both by SIMS and resistance measurements. They ranged from 1 to 3 microns. The CERN film had columnar grains 110+/-20 nm in diameter, and was somewhat textured, but mainly polycrystalline, according to GADDS. The CERN film thickness was 1.6+/-0.1 microns, as determined by SIMS. A layer of CuO was between the niobium and the copper substrate.

SIMS was done at the Surface Science Laboratory, University of Western Ontario, London, Ontario, Canada. A Cameca IMS-3f ion microprobe used a positive Cs ion beam. Negative secondary ions were monitored, with CsN giving an indication of the nitrogen present in the film. Depth scales were obtained using a Tencor P-10 surface profilometer.

ESTIMATE OF IMPURITIES FROM SIMS

The DESY bulk niobium sample was machined at Cornell into a rectangular shape and chemically polished with BCP to remove about 100 microns.

#hand@ccmr.cornell.edu
*CCMR=Cornell Center for Materials Research, REU=Research Experience for Undergraduates

The SIMS measurements near the surface are shown below in Figure 1. (1000 seconds corresponds to about 65 nm depth.) At a much deeper point, > 1 micron, the oxygen and carbon counting rates became constant, and presumably have become asymptotic. Assuming a normal state resistivity of .044 μΩcm after a small correction for a phonon contribution, we can use the ratio of oxygen counts to carbon counts to estimate the concentration[5] of carbon as < 56 ppm and of oxygen as < 44 ppm. The inequalities are used because other possible impurities, including Ta, are neglected.

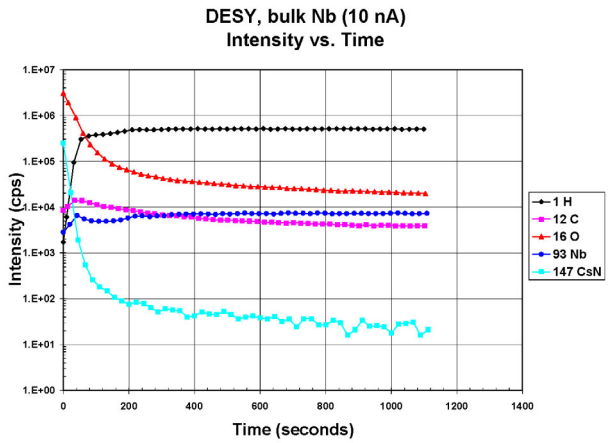

Figure 1: SIMS of bulk Nb, surface to 70 nm deep

For comparison, Fig. 2 below shows a SIMS plot over the same depth range for the CERN niobium film on copper.

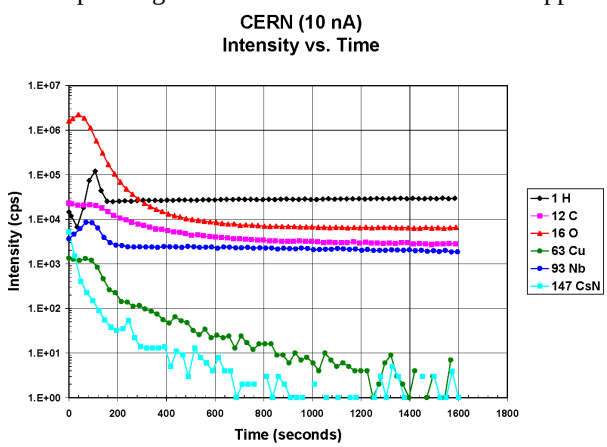

Figure 2: SIMS of Nb/Cu, surface to 100 nm deep

For SIMS at a point 1-2 microns from the surface, we take ratios of oxygen/niobium, carbon/niobium, hydrogen/niobium and compare these to the same ratios for the bulk DESY sample. This eliminates some systematic errors. We can make up the following table for the various element ratios relative to the bulk sample.

FILM	RRR	O	C	H
CERN	11.5	5.9	2.6	0.3
Film 19	-	2	0.8	0.02
Film 29	4.1	38	38-73	0.08
Film 30	65.3	1.9	2	0.15

Table 1: Ratios of elements in films to bulk ratios

The errors on O and C are 10-15%, on H 50%

MAGNETOMETER RESULTS FOR THE LOWER CRITICAL FIELD H_{C1}

Magnetization measurements were done at Cornell on a Quantum Design MPMS SQUID magnetometer. The curves[6] of magnetic moment m(H) vs. applied parallel magnetic field H for the DESY and CERN samples are shown in figures 3 and 4.

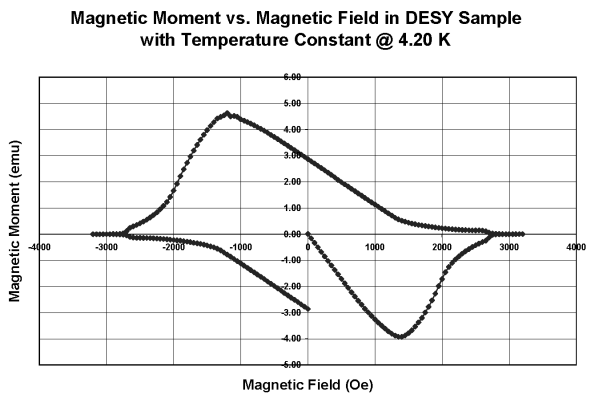

Figure 3: m(H) for DESY bulk Nb sample

A clearly visible break in the slope of m(H) is visible in all four cases we measured (DESY,CERN, film 19, film 30). Straight lines were fitted to either side of this break, and H_{c1} determined as the intersection of these lines[7]. In the case of all of the films, this break is very well defined, and the error on H_{c1} is very small. In the case of the DESY sample, demagnetization effects round the transition,but we could still determine H_{c1}.

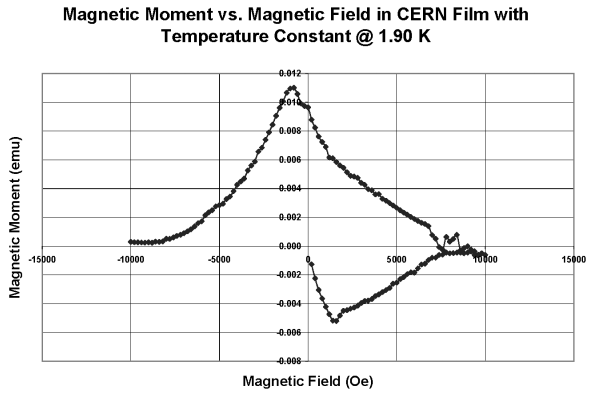

Figure 4: m(H) for CERN Nb/Cu Film

H_{c1} is directly related to cavity performance, setting the effective maximum attainable accelerating gradient of the cavity. For a cavity of the TESLA design, the RF magnetic field is 42 Oe/MeV/m[8], so we can convert the measured value of H_{c1} into a theoretical maximum accelerating gradient. This is tabulated below in Table 2. (In the table, $E_{av}= H_{c1}/42$ MeV/m.)

Sample	H_{c1}(1.9K) [Oe]	E_{av}[MeV/m]
Pure Nb[9]	1676	39.9
DESY	1653 +/- 70	39.4
CERN	1471 +/- 60	35.0
Film 19	1454 +/- 80	34.6
Film 30	1946 +/- 50	46.3

Table 2: H_{c1} and maximum attainable gradient

In the table above, for comparison, we also give the value of H_{c1} for ultrapure niobium[9]. (RRR=1600+/-400).

These numbers correspond closely to what is actually observed in the best cavities. We believe a magnetometer measurement of the lower critical field is a simple and inexpensive way to predict the upper limit of acceleration. Flux entry into the superconducting cavity wall will lead to excessive heat and thermal breakdown. The relatively high value of H_{c1} for the film 30 is probably related to the relative lack of surface oxidation (compared to the other films) and also perhaps may be due to a difference in the composition of niobium suboxides and oxyhydrides near the surface.

Other measurements with the magnetometer

The upper critical fields H_{c2} and in some cases H_{c3} were also measured. They will be the subject of a longer report[10]. The even part (irreversible) of the magnetization curve taken by starting with $H>H_{c2}$ is a measure of the pinned vortices in the film or bulk sample. The bulk sample has a much lower density of pinned vortices at H=0 than any of the films, indicating a higher density of pinning sites in the films. In the Cornell films, which have no grain boundaries, these must be defects or voids. TEM pictures of the CERN film[11] indicate a high

density of both defects and voids besides the columnar grain boundaries. These defects might be reduced by annealing, thereby reducing the coupling of fluxons to the lattice. This coupling is a potential source of heat and thus thermal breakdown.

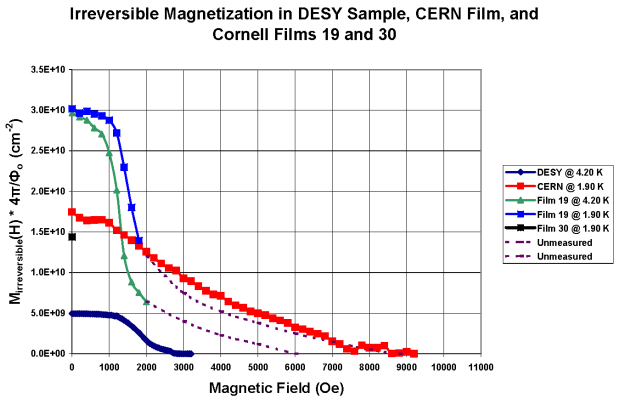

Figure 5: Irreversible Magnetization vs. H

From the value of H_{c2} and the thermodynamic critical field[7] one can determine the electromagnetic penetration depth. At 1.9 K, the value of λ for the DESY sample is 30.4 nm, for film 30 is 34.9 nm, and for the CERN film is 55.1 nm.

The normal conducting mean free paths are: DESY: 868 nm, film 30: 169 nm, and CERN: 27.7 nm. This does not include any contribution from phonon scattering.

CONCLUSIONS AND NEW DIRECTIONS FOR FILM-BASED CAVITIES

Sputtered niobium films produced at Cornell and CERN do not have the same superconducting properties as bulk niobium used at DESY. Films must have lower concentrations of impurities and defects to compete with bulk cavities. Low hydrogen content is essential, since hydrogen creates defects at low temperatures.

In the future, films must possess an H_{c1} at least as high as for pure bulk niobium. If the surface is smooth and protected from wet oxidation[12], H_{c1} for films can be significantly higher than achieved in the bulk case. We speculate that it may be possible to achieve higher gradients than at present with the right surface treatment.

TEM pictures showed a high density of defects and voids in the CERN film. There is indirect evidence (see fig. 5) that many defects exist in the epitaxial films also. The pinning site density was measured using the H=0 value of the upper branch of the magnetization curve. The density of trapped vortices in the CERN film is about four times greater than in the bulk DESY sample. Perfectly annealed high RRR bulk niobium with low hydrogen content shows little or no hysteresis[6]. $M_{irreversible}=0$ in the latter case.

Annealing at high temperatures is not possible with copper cavities. However, niobium films deposited on molybdenum cavities could be annealed at very high temperatures. Nb/Mo cavities should perform as well as the bulk, at a considerable saving in the amount of ultrapure niobium required. The molybdenum thermal conductivity at low temperatures is considerably higher than superconducting niobium, and should be sufficient for accelerator applications.

For satisfactory performance of film-based cavities, it is not necessary to produce epitaxial films, but the grain size should be > 3 microns after annealing.

If these criteria are obeyed, and the surface of the niobium is sufficiently smooth, gradients and Q values should be equal to or better than cavities made of bulk niobium.

Acknowledgements

This work was supported in part by the Cornell Center for Materials Research (CCMR), a Materials Research Science and Engineering Center of the National Science Foundation (DMR-0079992). It was also supported by a National Science Foundation SGER Grant DMI-0226076.

Particular acknowledgement is made of the use of the CCMR Facilities: the Materials Facility, the X-Ray Diffraction Facility , the Research Computing Facility, and the Center for Nanoscale Systems (CNS) Device Characterization Facility. We also would like to thank the following individuals: Prof. Bruce van Doren, Sara Barron, Darren Dale, Ron Kemp, John Sinnott, John Hunt, Dr. Maura Weathers , Jonathan Shu and Douglas Milton. Dr. Sergio Calatroni of CERN kindly provided the Nb/Cu film and an unpublished draft manuscript. Thanks also go to Dr. Helene Schember and Prof. Frank DiSalvo of CCMR for their encouragement and support.

REFERENCES

1. Provided by Dr. Axel Mattheisen of the DESY TTF Group.
2. C. Benvenuti, et al, Physica C **351** (2001), 429
3. Dr. Sergio Calatroni, CERN, private communication. Our film is film “B” in the Table I of the publication, ref. 2.
4. GADDS=**G**eneral **A**rea **D**etector **D**iffraction **S**ystem. A facility operated by CCMR.
5. H. Safa, et al, Journal of Alloys and Compounds, **232** (1996),281
6. K. Saito and M. Wake, Proc. 7 th Workshop on RF Superconductivity, SRF1995, 553-557
7. H.W. Weber et al, Physica C **161** (1989), 272-293. See also ibid Phys.Rev. **B44**(1991), 7585.
8. H. Padamsee, private communication.
9. D.K. Finnemore et al, Phys.Rev. **149**(1966), 231.
10. To be published.
11. TEM pictures were made by Dr. Fred Pearson of the Brockhouse Materials Science Institute at McMaster University, Hamilton, Ontario, Canada
12. See paper submitted to this workshop by W.R. Frisken and L.N. Hand entitled *“Wet Oxidation of an Epitaxial Film”*