

NIOBIUM SURFACES FOR RF SUPERCONDUCTORS*

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Introduction

At temperatures below 2° K, niobium has challenging potential for use in superconducting electron linear accelerators and rf particle separators. To date, this potential has not been fully realized, although two superconducting linacs are under construction.^{1,2} Measurements on experimental superconducting cavities^{3,4} have shown that it is possible to obtain very low residual surface resistance values ($R_{\text{res}} < 8 \times 10^{-9}$ ohms) and reasonably high critical magnetic fields ($H_c^{\text{AC}} \approx 1000$ Oe). However, in order to obtain these "good numbers" with cavities fabricated from commercial electron beam melted niobium, elaborate recipes have been worked out for machining, chemically and/or electrochemically polishing, ultrahigh vacuum high-temperature outgassing, and/or anodizing. Most of the treatments in current use are variations of processes developed by Turneure and Weissman³ and Martens, Diepers and Sun.⁵

While these processing recipes sometimes yield acceptable values of surface resistance and breakdown field, the success rate at SLAC^{6,7} has not been high. Furthermore, once a cavity exhibits low rf residual losses, it does not retain this property. Exposure to air causes degradation. In the case of anodized surfaces, even good vacuum (10^{-7} Torr) does not prevent degradation.⁸

Little information has been developed relating changes in surface chemistry and morphology to variations in the rf superconducting properties of interest. Halbritter⁹ has proposed a model of surface fissuring which can explain some of the residual loss behavior, and Rabinowitz¹⁰ has derived the correct frequency and temperature dependence of residual loss based on a model of normal regions near the surface. An additional suggestion is developed here that hydrogen sorption is responsible for much of the scatter in the superconducting cavity measurements. This idea is reinforced by the outgassing behavior and surface characterizations recently begun.

Surface Topography

In an effort to optimize surface smoothness and understand what changes occur during the preparation of the niobium, examinations of the surface were made following machining, chemical etching with HF-HNO₃, heating in vacuum to 2500° K, remachining, re-etching, anodizing, etc. The results of examination using both optical and scanning electron microscopy can be summarized as follows:

Surface and grain boundary topography are greatly altered by the order and extent of the processing steps. In order to minimize "orange peel" and "grain boundary ghosting,"¹¹ it was necessary to heat the niobium to the highest processing temperatures—to enable large grain growth—before final machining. Otherwise the original smaller grain boundaries produce etch rifts and this topography can be preserved through many etching and heating cycles.

Grain boundary stepping and channeling can be very pronounced due to both thermal and chemical etching. What effect the observed grain boundary grooves, channels, pits, and steps have remains to be explored. In the one case where a cavity was fabricated from a single crystal¹² very poor results were obtained.

Surface Chemistry

It is known from recent developments with Auger spectroscopy^{13, 14} that surface segregation of some impurities occurs when refractory metals are heated. These workers and others¹⁵ have also shown that oxygen persists on niobium surfaces up to temperatures > 2300° K. Until recently, it was generally believed that surface oxides might contribute to the residual losses. However, recent success in producing high Q cavities with anodic Nb₂O₅ coatings^{8, 16} has shown that this is not the complete story. In fact, the loss tangent has been shown to be less than 10⁻⁵ at 2.6 GHz.¹⁷ The same surfaces examined by SEM were also analyzed using

a cylindrical mirror-type Auger spectrometer. The results can be summarized as follows:

1. No evidence of metallic impurities was found on any surface.
2. Oxygen was present on all surfaces and was still evident after removing 60 Å by argon ion bombardment. 60 Å is the reported thickness¹⁸ expected for the natural oxide.
3. Fluorine was evident on those surfaces which had been HF-HNO₃ etched and not heated in vacuum.
4. Carbon was present on all surfaces to some extent but could be reduced to low values by argon bombardment. Also carbon was found distributed non-uniformly. Examination by electron microprobe confirmed this and showed evidence of carbon clumping at grain boundaries.
5. Only minute traces of nitrogen were seen on all surfaces, even on the surface examined following heating in vacuum to 2500^o K, let up to pure nitrogen, and stored in nitrogen. (This is the standard procedure used with the microwave cavities.)

These results are also consistent with Auger and Leed studies,¹⁴ which show little nitrogen absorption on low-index niobium planes. It is obvious that exposing the high-temperature-cleaned niobium surface to nitrogen at room temperature does not protect it in any way from subsequent reaction with more active gases.

Niobium Outgassing

An induction-concentrator type ultrahigh vacuum furnace was used to vacuum-thermal process X-band size niobium cavities and samples. The salient features of this apparatus are:

1. Temperatures up to 2700° K easily attained and maintained.
2. Maximum sample size, 5 cm dia \times 8 cm long (\sim 1.3 kg of niobium).
3. Only the sample and its supporting niobium rod get hot, permitting measurement of sample outgassing with minimal extraneous effects.
4. The system is ion-pumped, bakeable, and reaches base pressures of $\sim 2 \times 10^{-11}$ Torr with the sample cold.
5. With a cavity at temperature (2500° K) for times greater than 40 hours, total pressures of $3 - 4 \times 10^{-9}$ Torr can be attained.
6. A quadrupole mass analyzer permits continuous monitoring of partial pressures.

During the course of outgassing and re-outgassing many X-band cavities, the following were noted:

1. When heating begins, H_2O , CO_2 , CO , and H_2 are evolved.
2. H_2 is the dominant species evolved between 700° and 1800° K, with peaking occurring around 1500° K.
3. CF transients are observed to occur between 1000° and 1200° K. This is undoubtedly the way the fluorine is removed from the surface and grain boundaries.
4. Above 1500° K, CO evolution becomes significant. However, CO usually falls to low levels ($< 10^{-9}$ Torr) after minutes above 2000° K.
5. Above 1800° K, N_2 is the dominant species and remains so for days at 2500° K.
6. H_2 persists at the 10^{-9} Torr level when the sample is at 2500° K, probably due to other sources including $H_2 - N_2$ surface exchange reactions.
7. Finally, and most important for the present argument, when cavities were re-outgassed following exposure to ambient conditions, no decrease in the total amount of hydrogen evolved was noticed, although CO and N_2 evolution

was significantly reduced for successive outgassings. In fact, sometimes the hydrogen load appeared greater on second, third, or fourth heating following atmospheric exposure. Bulk chemical analysis of niobium samples before and after outgassing at 2300° K confirmed the above observations. Carbon was reduced from 0.023 to 0.015 atom percent, N was reduced from 0.028 to 0.015 atom percent, oxygen was reduced from 0.040 to 0.023 atom percent, whereas hydrogen showed an increase from 0.033 to 0.035 atom percent.

Hydrogen Indictment

The excellent review paper by Chandler and Walter¹⁹ shows the literature on the niobium-hydrogen system to be disparate, especially with regard to adsorption, desorption, solubility, and diffusion rates at low temperatures. All investigators have noted the profound effects of gas purity and surface condition on all these rate processes.

Measurements of hydrogen sorption by evaporated niobium thin films²⁰ have shown hydrogen to be taken up to near Nb H_{0.5} both at 77° and 300° K. Sorption rates at the lowest temperature were steadily higher.

Crude preliminary measurements were made at SLAC wherein a cylinder of niobium (~ 700 grams) was outgassed in the induction furnace for 17 hours at 2400° K (a typical X-band cavity cycle). Following cooldown to room temperature, the chamber was let up to hydrogen at 0.2 Torr. By measuring the change in pressure over 24 hours, some estimates of uptake ($C \sim 0.05$ atom percent) and early sticking probability ($S \sim 0.03$) were made. Chemical analysis performed somewhat later showed the hydrogen concentration to be 0.08 atom percent. Following this hydrogen treatment, the cylinder was measured for changes in normal state resistivity ratio $\rho_{300^{\circ} \text{K}}/\rho_{4.2^{\circ} \text{K}}$ by an induction method.²¹ The outgassed-hydrogen-exposed cylinder showed an increase in resistivity ratio approximating that to be expected from the outgassing treatment alone, which suggested that the hydrogen

taken up may be concentrated near the surface and not diffused very deeply in the bulk. This conclusion is supported by the fact that the critical magnetic field (H_{c1}) was reduced by the treatment.

With our microwave cavities, if hydrogen concentrates near the niobium surface (the rf supercurrents are carried $\sim 500 \text{ \AA}$ deep), electrons may be donated to the band structure of the metal²² increasing the electron-to-atom ratio, thereby decreasing the transition temperature²³ and increasing the residual surface resistance. Recent studies²⁴ of hydrogen uptake by niobium at moderate temperatures ($360^\circ - 1000^\circ \text{ K}$) show large changes in resistivity as hydrogen is adsorbed and dissolved. The greatest change in resistivity per unit hydrogen sorbed occurred at the lowest temperature investigated (360° K).

Viet²⁵ made the observation that when large gas bursts were noted when "pinching off" experimental niobium cavities, high rf superconducting surface resistances were obtained. Although no residual gas analyses were performed, it is probable that hydrogen was released during the pinch-off operation.

Oakwood and Daniels²⁶ found that chemical etching greatly reduced the sorption of hydrogen. This may explain why cavities tested immediately after etching yield moderately low surface resistance values.

Cavity preparation by chemical etching, followed by heating to high temperatures $\sim 2400^\circ \text{ K}$ in ultrahigh vacuum, is certain to produce the most hydrogen-avid surface. Furthermore, "letting up to," transferring, and assembling in nitrogen—because it is not chemisorbed—does not provide a barrier to the more active gases which eventually react with the surface. Due to the ubiquitous nature of hydrogen, i. e., present in the atmosphere ($\sim 4 \times 10^{-4} \text{ Torr}$) produced in reaction with water and usually the dominant residual gas in vacuum chambers, it is extremely difficult to prevent hydrogen exposure. Therefore, some method must be used to prevent the niobium surface from sorbing hydrogen.

Stabilizing the Surface

Current efforts with surface coating niobium center on anodizing^{5,8} and nitriding.²⁷ Alternatively, more stable surfaces might be niobium monocarbide or carbo-nitride.²⁸

In addition, instead of trying to prevent oxygen exposure of processed cavities, one might try to let up to pure oxygen and let the pure oxide form, which is known to be a barrier to hydrogen in the case of zirconium oxide.²⁹

Most of the foregoing is speculation; the critical experiments remain, and will be done in the near future.

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