

# TEM STUDY OF NIOBIUM SURFACES TREATED BY DIFFERENT POLISHING TECHNIQUES\*

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## Abstract

Transmission Electron Microscope (TEM) cross-section observation on niobium (Nb) surfaces has been a challenge to our superconducting radio frequency (SRF) community due to the highly reactive nature of Nb. Although it was demonstrated in an early attempt [1] that under a suitable sample preparation procedure reasonably clear cross-section images of Nb could be obtained, to the best of our knowledge good atomically resolved images had never been obtained. In this report, it is shown that by modifying the sample preparation procedure adopted in reference 1 it is possible to obtain good cross-section images of Nb surfaces with atomic resolution routinely. Surface atomic structures of Nb samples prepared by buffered electropolishing (BEP), buffered chemical polishing (BCP), and an untreated sample will be reported and compared.

## INTRODUCTION

TEM is a well known microscopic instrument widely used in different areas for examining microstructures of materials down to atomic level. For our Nb SRF community, microstructures are very important especially on Nb surfaces or the region within 50 nm of the surfaces since typical RF penetration depth of Nb at 1.5GHz is 50 nm. Defects and imperfections in this surface region may degrade RF performance of Nb SRF cavities. Understanding the formation mechanism of the defects and imperfections and minimizing them are an important task facing all the researchers in the SRF field.

In the past, no many attempts were made on TEM observations of Nb due mainly to the difficulties in sample preparation since Nb is highly reactive in air. To the best of our knowledge, only one successful attempt [1] was made for doing TEM cross-section observation on polycrystalline Nb employing the conventional sample preparation procedures with ion milling technique, whereas two attempts were done on Nb thin films [2] and single crystals [3] employing Focused Ion Beam (FIB) technique. In all cases, no atomically resolved images were obtained. In this report, it is shown that by modifying the sample preparation procedures adopted in reference 1 we can obtain routinely atomically resolved TEM cross-section images of Nb. Measurements were

done on samples treated by BEP, BCP, and a reference untreated sample.

## SAMPLE PREPERATION

Nb samples used in this study were taken from the same Nb sheet. Then samples were separated into three groups, one for treatment by BEP [4], one for BCP, and the other for using as reference untreated samples.

BEP treatment was done employing the simple setup described in reference 4. BCP was done using the conventional 112 acid mixture. At least 150  $\mu\text{m}$  was removal from the original Nb surfaces for both BEP and BCP treated Nb samples. After the chemical treatments, the samples were first rinsed with DI water for half an hour followed by ultrasonic cleaning with micro and then rinsed again with DI water. Finally water on sample surfaces was blown away by dry nitrogen gun.

TEM sample preparation was done in a conventional way and will be described in some details here, especially since other institutions had not succeeded in doing the same up to now. The procedure described here allows us to obtain routinely atomically resolved Nb surface cross-section images. Hopefully this will enable other researchers who have not much TEM sample preparation experiences to have some ideas on how to repeat what we

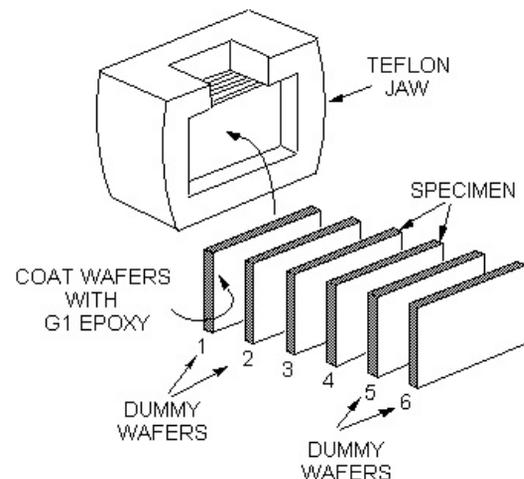


Figure 1: Illustration on how to put Nb samples and dummy wafers together by G1 epoxy and then put them into a Teflon Jaw.

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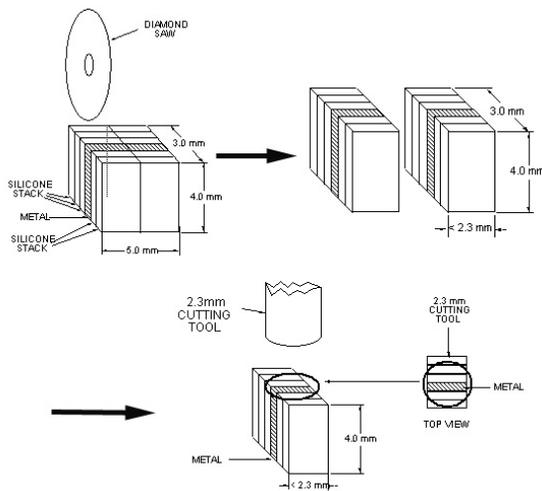


Figure 2: Illustration on the steps to obtain Nb cross-section columns.

did and to try to do TEM sample preparation and observation themselves.

Nb samples are first cut into a suitable size by a diamond cutter (LECO VC-50). Then the samples (usually 3 or 4 mm thick) have to be thinned to 0.5 mm thin using a semiautomatic lapping device such as, for instance, ECOMET 4 Grinder-Polisher Buehler. Afterwards, the thin Nb samples are cut into 4X5 mm rectangular pieces (called here as dummy wafers) using a cutting tool such as Model 601 made by Gatan with a rectangular cutter. Should cut some standard commercial Si wafers into the same rectangular pieces by using for instance Model 360 made by South Bay Technology, Inc. Then stack the two Nb samples and four dummy wafers together using G1 epoxy (dissolvable in acetone) made by Gatan in the way shown in Figure 1 where the Nb surfaces that need TEM cross-section observations are glued together face to face. The sample stack is cured on a hot plate at 130 °C for 10 minutes under a certain applied pressure to make the bonding better. Then follow the steps shown in Figure 2 for getting an Nb column by changing the head of the cutting tool (Model 601 by Gatan) into a circular cutter with a diameter of 2.3 mm. Then the sample column is cut into some 500 μm discs approximately. Then follow the steps shown in Figure 3 for

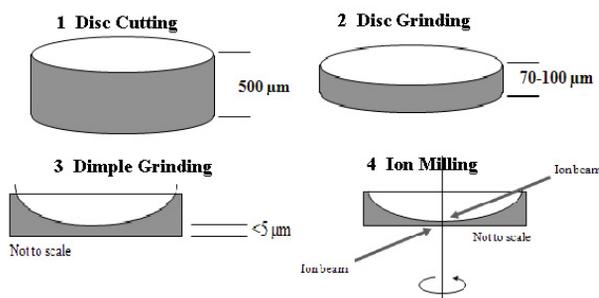


Figure 3: Illustration on the steps for getting final Nb TEM cross-section samples after the steps shown in Figure 2.

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getting the final TEM cross-section samples. There are two reasons why the Si dummy wafers are used here. One is for monitoring the thickness of the dimpling since Si becomes transparent under the light when it is less than 10 μm. The other is for supporting the weight of the dimpler head since Nb is so soft so that it would have bent if there were not the dummy wafers on its two sides.

It is important to spend a few more words on the final step of the sample preparation. Ion milling is very important regarding whether the final TEM observation is successful or not. We use Gatan PIPS Model 691 [1] for ion milling. The PIPS has a CCD camera with a TV monitor to view the polishing process continuously. The typically parameters used in ion milling are: a) The gun angle is 3.5~4 ° with respect to the horizontal line. b) Ion beam current is 40 μA. c) Beam modulation is turned on to avoid possible sample heating during ion milling. The ion milling stops at the point when the glue layer between the samples is gone.

EXPERIMENTAL RESULTS AND DISCUSSION

It is interesting to report some results from our earlier attempt [1] when using a similar sample preparation procedure as described here, but observed with an old JEOL JEM-100CX for comparison. The measurements were done on an Nb sample that was treated by the conventional electropolishing (EP) technique. Figure 1 shows a typical cross-section image. No detailed feature could be seen, except some possible surface layer that could be attributed to the well known Nb<sub>2</sub>O<sub>5</sub> layer as shown in Figure 4. Contrast became better at lower magnifications as typically shown in Figure 5.

The resolution of the images improved dramatically when a much better TEM JEM-2100F was employed for doing the observations. Figure 6 shows an atomically

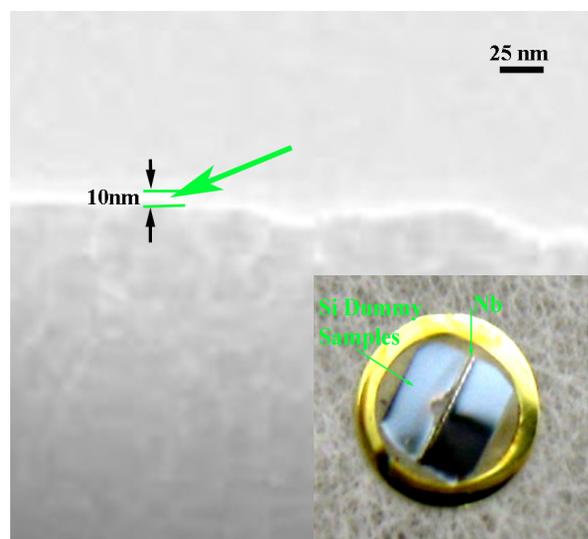


Figure 4: TEM cross-section image of an EP treated Nb sample surface obtained using JEM-100CX. The arrow indicates the possible surface oxide layer. The insert shows an example of TEM samples.

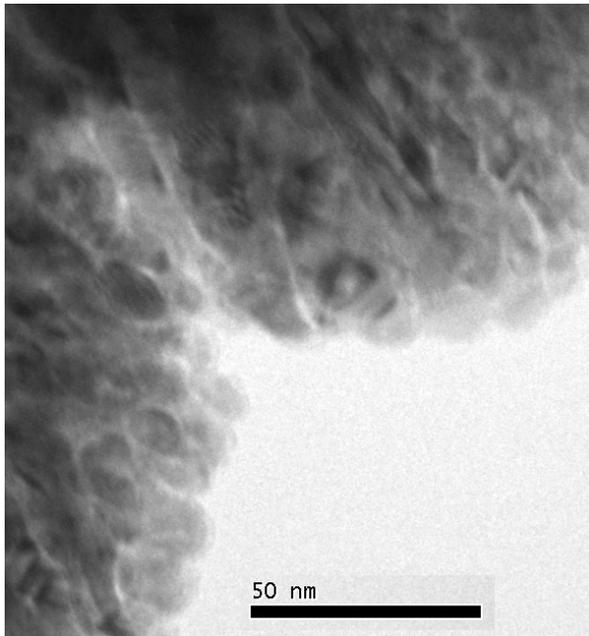


Figure 5: TEM cross-section image of an EP treated Nb surface obtained using JEM-100CX under a lower magnification than that of Figure 4 showing a better image contrast.

resolved surface cross-section image of an BCP treated Nb sample. From the contrast variation there, it is not difficult to assign the thickness of the surface oxide layer. It is only about 3 nm that is significantly thinner than what people used to believe. We can also see some defects near the surface as indicated by arrows. Arrow 3 indicates a location where the disorder structure of the oxide penetrates deeper into Nb bulk with a lateral scale about 1 nm. This can be a weak location for magnetic fluxes to enter the bulk of Nb, leading to a lower  $H_c$ .

TEM cross-section observation is the existence of a transition zone between the oxide zone and the bulk Nb area as indicated in Figure 6. This transition zone is better

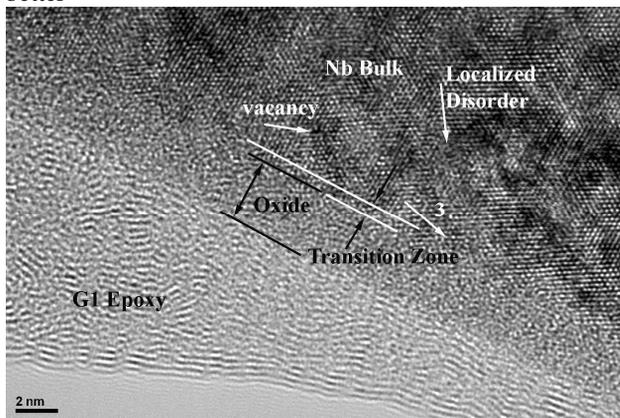


Figure 6: Atomically resolved TEM cross-section image of an BCP treated Nb sample obtained using JEM-2100F (see text for more details).

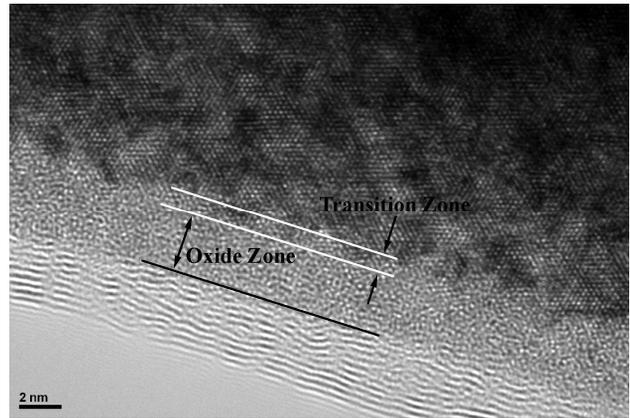


Figure 7: Atomically resolved TEM cross-section image of an BCP treated Nb sample that shows more surface area. The oxide layer and a possible transition zone between the  $Nb_2O_5$  and the bulk Nb is indicated.

viewed from Figure 7 where more surface area is shown. For the oxide zone, the contrast of the atoms is clearly different from the atoms in the other area. Furthermore, the atomic arrangement of this region appears to be the same under TEM and doesn't show regular structure. This is consistent with the conventional wisdom that normally the surface of Nb is covered by an amorphous  $Nb_2O_5$ . This fact can be further confirmed by performing a fast Fourier transform (FFT) of the atoms in zone as shown in Figure 8a. One can see clearly from Figure 8a the amorphous ring pattern, which is clearly different from an FFT done on the bulk Nb zone as shown in Figure 8b. A six-fold symmetry is clearly visible in Figure 8b implying that the atomic plan is [111].

We also attempted to do FFT on the transition zones of Figs. 6 and 7. It was not successful since very few lattices were involved in the FFT in these cases. We suspect that the transition zone may correspond to Nb sub-oxides such as, for instance, NbO or/and  $Nb_2O_3$ . From Figs. 6 and 7, we estimate that the thickness of the transition zone is about 7 Å, although it is not possible to clearly define the boundaries on either side.

The understanding of this transition zone is very important since the suboxides can have significant effect on the RF performance of Nb SRF cavities. The suboxides can show metal or semiconductor

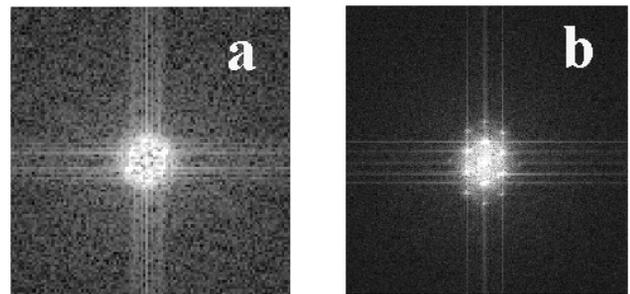


Figure 8: FFTs of a) the oxide zone and b) the bulk Nb zone shown in Figure 7.

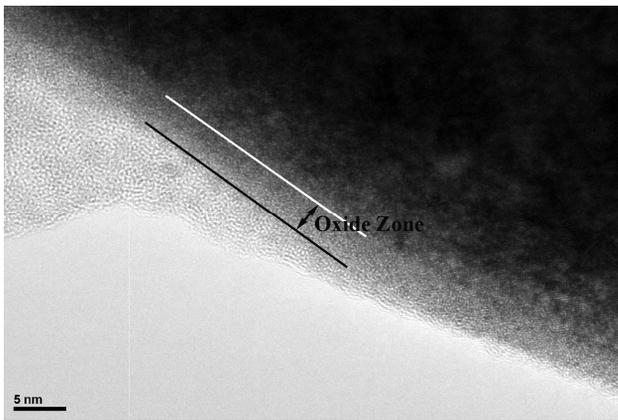


Figure 9: Typical TEM surface cross-section image obtained on an BEP treated Nb sample at a relatively low magnification in order to have a better contrast for the surface oxide layer.

characteristics that might cause substantial amount of RF losses at the operational temperature of the SRF Nb based accelerators. Sometimes they can be superconductors with a lower  $T_c$  than that of the bulk Nb due to the proximity effect, which can still contribute to the residual surface resistance of an Nb SRF cavity. They are ways to find out what the chemical composition is for the transition zone. One is a line EDX scan. But this may not be so sensitive to the oxygen concentration. The other is EELS. These measurements have yet to be done.

Figure 9 shows a typical TEM cross-section image obtained on an BEP treated Nb sample at a relatively low magnification in order to see the surface oxide layer clearly. The oxide zone is calculated to be 3 nm from Figure 8. Therefore, from these extremely high resolution TEM images we seem to find that the thickness of the surface pent-oxide layer of Nb samples treated by BEP is the same as that by BCP. This result agrees with the depth profile measurements reported in Ref. 5.

To see the possible transition zone, a picture of higher

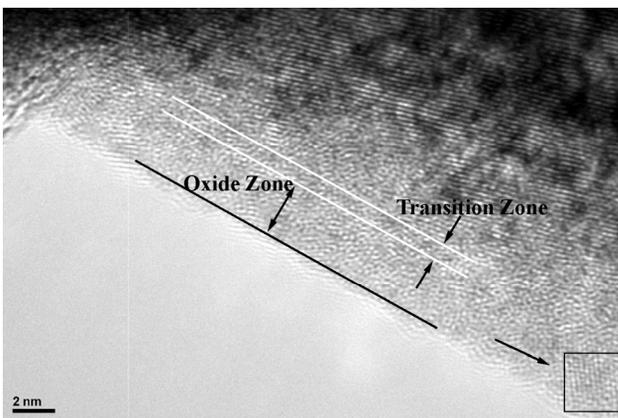


Figure 10: Typical atomically resolved TEM surface cross-section image of an BEP treated Nb sample. The arrow and box indicate a small area where some lattice structure is observed.

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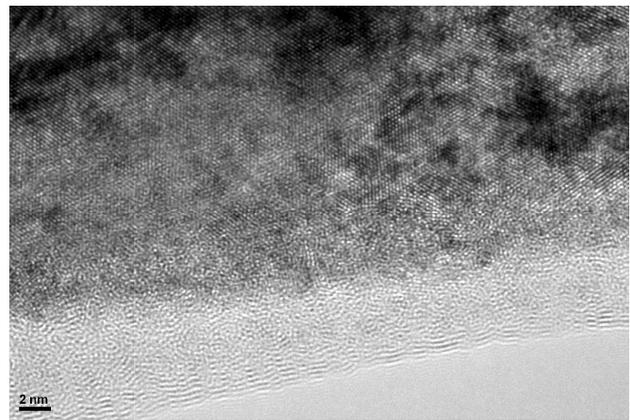


Figure 11: Typical atomically resolved TEM surface cross-section image obtained on an untreated Nb sample.

magnification is needed (Figure 10). Apart from the 3 nm oxide zone, the transition zone in this case appears to be about  $\frac{3}{4}$  of that of BCP treated Nb samples as typically shown in Figure 6. This observation seems to imply that the

RF performance of BEP treated cavities should be better than that of BCP treated cavities if the transition zone is Nb suboxides. In reality, however, currently the RF data of BEP are not significantly better than those of BCP treated samples and sometimes even worse [5,6]. How to understand this discrepancy? First, we have to be clear here that RF performance of an Nb SRF cavity does not depend solely on the suboxides. Other imperfections and surface residuals may have strong effects too. For instance, there is a regular lattice structure that is different of the lattice of the bulk appearing on the very top layer of the surface as indicated by the arrow and the square in Figure 10. What is the material? Is it a secondary phase? This type of materials can certainly degrade the RF performance if they are not superconducting at the operation temperature of an Nb based accelerator.

No much information can be extracted by the TEM images obtained on an untreated reference sample due to the fact that the surface was pretty rough even under the atomic level. It was difficult to determine the G1 epoxy/the oxide and the oxide/bulk Nb boundaries. A typical atomic cross-section image is shown in Figure 11.

It is interesting to point out here that for most of the atomically resolved TEM cross-section images we obtained the surface determination layer is [111] oriented. This cannot be simply attributed to coincidence since the samples under this study are polycrystalline with a typical grain size of 50  $\mu\text{m}$ . One likely reason for this can be that [111] surface is a close-packed surface that may be most resistant to the deterioration in air.

## CONCLUSION

This paper reported an TEM sample preparation technique that allowed atomically resolved Nb surface cross-section images to be obtained routinely. Preliminary results indicated that the Nb pentoxide layer

on the surfaces of BCP and BEP treated Nb was thin and was about 3 nm. A thin transition zone of less than 7 Å between the pentoxide layer and bulk Nb was found on BCP and BEP treated Nb samples that might correspond to Nb suboxide layer. More experiments especially from EELS and EDX are needed in order to confirm the existence of this transition zone that may be critical in understanding and optimizing the RF performance of Nb SRF cavities.

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