SIMS AND TEM ANALYSIS OF NIOBIUM BICRYSTALS

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Abstract

Interstitial impurities such as C, N, O and H on the Nb surface play a key role in the efficiency of superconducting radio frequency (SRF) cavities for particle accelerators. Thus, it is important to understand the behaviour of these interstitial impurities with respect to grain boundaries. The large single crystal grains in large grain Nb make it possible to select bicrystal samples that have a well defined grain boundary. In this work, Dynamic SIMS was used to analyze two Nb bicrystal samples, one of them heat treated and the other chemically treated by buffered chemical polishing (control). H levels were found to be higher for the control sample and a difference in the H intensity and sputtering rate was also observed across the grain boundary for both samples. Transmission Electron Microscopy (TEM) was used to study the bicrystal interface and the surface oxide layer. The interface showed no discontinuity and the oxide layer was uniform across the grain boundary for both samples. TOF-SIMS imaging was also performed to analyze the distribution of the impurities across the grain boundary in both samples. C was observed to be segregated along the grain boundary for the heat treated sample, while H and O showed a difference in signal intensity across the grain boundary. Crystal orientation appears to have an important role in the observed sputtering rate and impurity ion signal differences, both across the grain boundary and between samples.

INTRODUCTION

Nb has become the material of choice for superconducting radio frequency (SRF) cavities due to its high critical temperature (9.2 K) , high critical magnetic field (200mT) and easy formability, that is, it can be molded to a cavity shape, which is extremely important from the manufacturing aspect. It is known that polycrystalline Nb tends to harbor interstitial impurities such as C, N, O, and H, which play an important role in the RF losses of these cavities. The presence of such impurities near the surface is particularly detrimental given that the penetration depth of the RF field is of the order of 40 nm.[1]

Initial experiments using Dynamic Secondary Ion Mass Spectrometry (SIMS) have shown that heat treated large grain Nb has lower H levels on the surface compared with non heat treated Nb, and that the cavity efficiency is seen to improve with heat treatment.[2,3]

Figure 1 shows mass spectra from two Nb samples, one with no heat treatment, just chemical etching by buffered chemical polishing (BCP), and one which was heat treated at 800^{o}C for 3hrs and then baked at 120^{o} C for 24hrs. The non heat treated sample mass spectrum in Fig 1(a) shows very intense peaks for the negative ions NbH^{-}, NbH$_2^{-}$, NbH$_3^{-}$, NbH$_4^{-}$, NbH$_5^{-}$ which indicate the presence of a high level of H and an affinity of Nb for H. These peaks dramatically decrease and the higher H containing ions vanish for the heat treated sample as shown in Fig. 1(b). Thus, heat treatment plays a very important role in controlling H levels in Nb. This is a known issue related to SRF Nb cavities [4]: heat treatment is part of the standard preparation procedure but a chemical etching is typically done after the heat treatment. Hydrogen can still be absorbed during the chemical treatment and its high concentration near the surface may still impact the cavity performance. Initial experiments were confined to an analysis area within a particular grain and the effects of grain boundaries on Nb-impurity element dynamics were not taken into account. Since it is known that grain boundaries are more susceptible to diffusion of impurity elements, it is important to study them. Thus, the current work focuses on the characterization of H, C, O and N at the grain boundary and near grain boundary regions of Nb bicrystal. Crystal orientation of these bicrystals was determined using Electron Back Scattering Diffraction (EBSD). Difference in crystal orientation was observed for the two crystals of both heat treated and control bicrystal samples. Dynamic SIMS was used to analyze the near grain boundary regions and Time of Flight SIMS (ToF SIMS) imaging was used to observe the presence of C, H , O and N right at the grain boundary interface. Transmission Electron Microscopy was also used to study the grain boundary interface and the surface oxide layer of both the Nb bicrystals.

EXPERIMENTAL

Samples of 7mm x 5mm x 2mm dimensions were cut by wire electro-discharge machining from large grain polycrystalline Nb disc in such a way that the grain boundary divided the sample into two parts, with each part being a separate crystal and having a distinct crystallographic orientation. The samples were chemically etched by BCP to remove about 80 µm of material from each surface, then they were heat treated in a vacuum furnace at 600 °C for 10 h, followed by 20 µm chemical

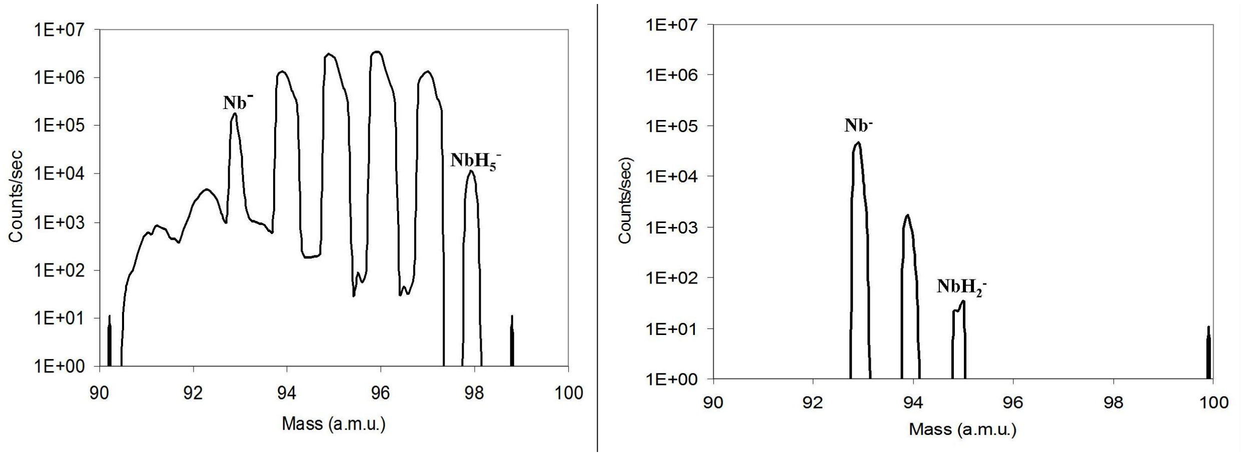

FIGURE 1: SIMS mass spectra showing difference in H between (left) non-heat treated and (right) heat treated sample.

etching by BCP. These treatments are commonly used for the preparation of SRF Nb cavities.

Since accurate SIMS measurements require surfaces with roughness of the order of 1 nm, the samples were "nano-polished" using a proprietary chemical-mechanical polishing at Wah-Chang. One of these samples was then heat treated at 800° C for 3hrs and then cooled to 120 °C for 24 hrs in a vacuum furnace. The other sample was used as is and was thus named "control". EBSD was carried out on both the samples using a TSL/EDAX machine with OIM analysis software to determine the crystallographic orientations of both crystals in each sample.

A CAMECA IMS-6F magnetic sector SIMS was used to perform surface analysis of the near grain boundary regions of the samples. Typical analysis conditions included a Cs^+ primary ion beam with 14.5keV impact energy and a beam current of 20nA. The raster area was fixed to be 120 x 120 µm with a detected area of 30µm diameter.

Surface imaging was performed at the grain boundary using an ION-TOF 5 ToF SIMS instrument with a Cs^+ sputter beam at 10keV impact energy and a 20nA beam current with a 180 x 180 µm raster area. A Bi^{3+} beam was used for analysis with a 0.7pA current, 100 x 100 µm detected area and 25keV energy.

Finally, TEM of the bicrystal samples was carried out with a Hitachi HF-2000 microscope. Focused Ion Beam was used to prepare the samples for TEM analysis using a FEI Quanta 200 3D instrument with a Ga^+ ion beam.

RESULTS AND DISCUSSION

Figure 2 shows the EBSD data obtained from the control (left) and the heat treated (right) samples. The color coded plot shows that the left crystal has (001) orientation while the right crystal has higher orientation indices for both the samples. The corresponding inverse pole figures show the orientation distributions observed for the respective crystals.

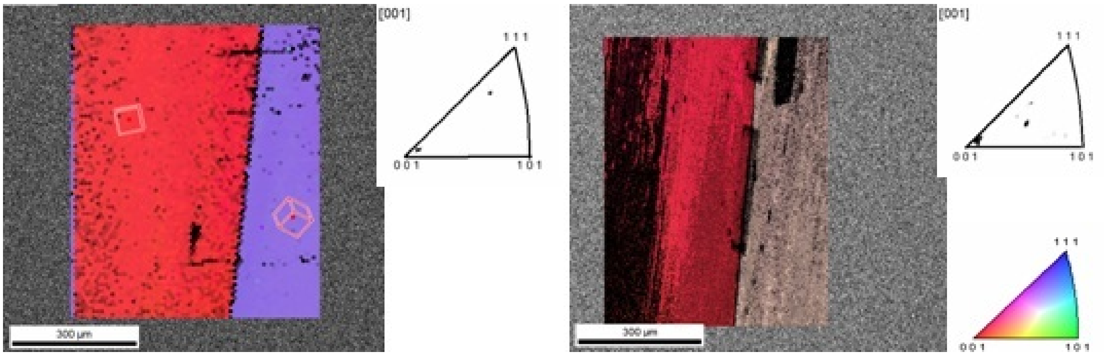

FIGURE 2: EBSD results for control (left) and heat treated (right) bicrystal samples. Color coding similar for both samples.

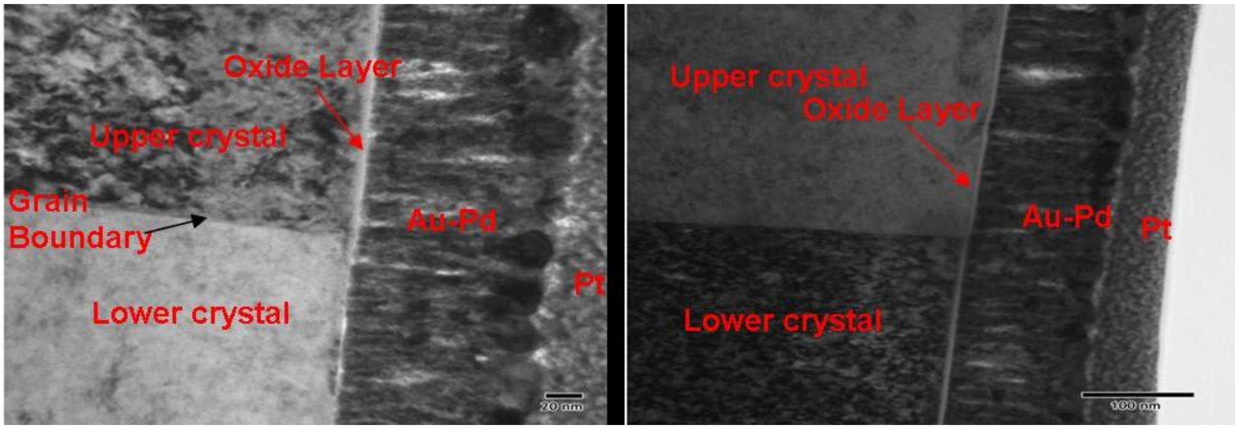

FIGURE 3: TEM micrographs of control (left) and heat treated (right) bicrystal samples.

Figure 3 depicts the TEM bright field micrographs of the samples. It is seen from these micrographs that the grain boundary interface is uniform with no discontinuity. The oxide layer also shows uniformity across the grain boundary and a thickness of 5nm on the surface for both the control and heat treated bicrystal samples.

Dynamic SIMS was used to characterize the surface of the near grain boundary regions for both samples. Measurements showed little to no changes in the C, O and N levels across the grain boundary and between samples which is in accordance with our previous work where we saw that the concentration of these species is sufficiently low that we expect them - not play a significant role in the efficiency of SRF cavities [5,6]. However, H levels were significantly different both within the bicrystal samples and between heat treated and control samples. H is extremely mobile in Nb which is why a quantitative estimate of H in Nb using SIMS is rather difficult, but a comparative study is possible using this technique [7]. Figure 4 shows the H/Nb intensity extracted from the SIMS measurements. As seen in the figure, H/Nb intensity varies within the same sample for both samples. This may be attributed to the difference in the crystallographic orientations in the two crystals, which further causes a difference in the sputtering rates. Notably, the sputtering rate difference between the two crystals of the control sample is almost a factor of three. Also, as seen in previous measurements, the control sample tends to harbour more H on the surface than the heat treated sample.

For imaging across the grain boundaries, TOF-SIMS imaging was conducted to a total depth of 0.25µm. Interesting results were seen for the interstitial elements, especially carbon. Figure 5 shows the ion images for the control (left) and the heat treated (right) samples. C seems to be segregated at the grain boundary for the heat treated sample and depleted around the grain boundary region, unlike the control sample, indicating that the heat treatment process causes diffusion of C into the grain boundary from the surrounding areas. No other interstitial element segregation was seen, although, the difference in the H intensity is in accordance with the dynamic SIMS results, where H shows high intensity in the control sample as compared to the heat treated sample. Again, the intensity difference across the interface for both samples could be an effect of the sputtering rate difference owing to the different crystal orientations. This effect is observed to some degree in all the species analyzed.

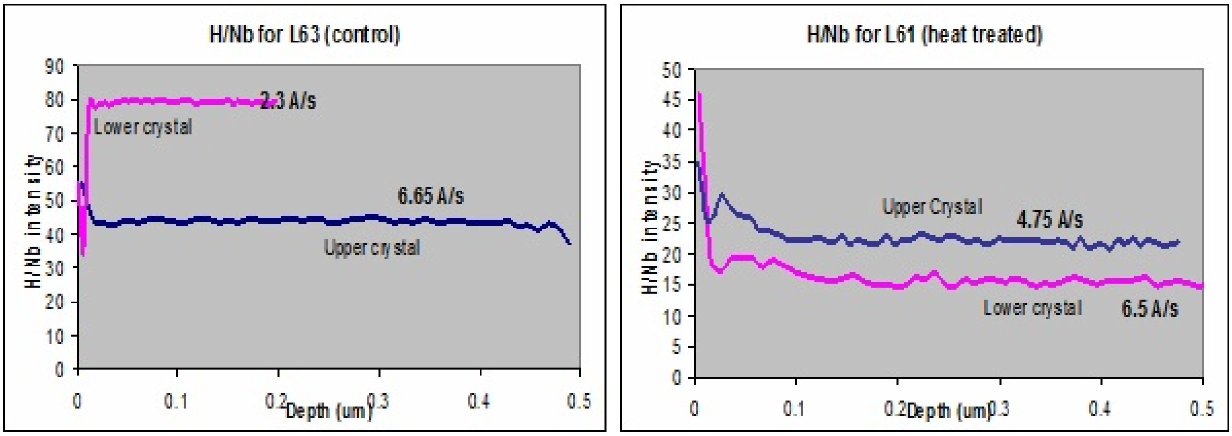

FIGURE 4: H/Nb intensities for control (left) and heat treated (right) samples extracted from the dynamic SIMS measurements.

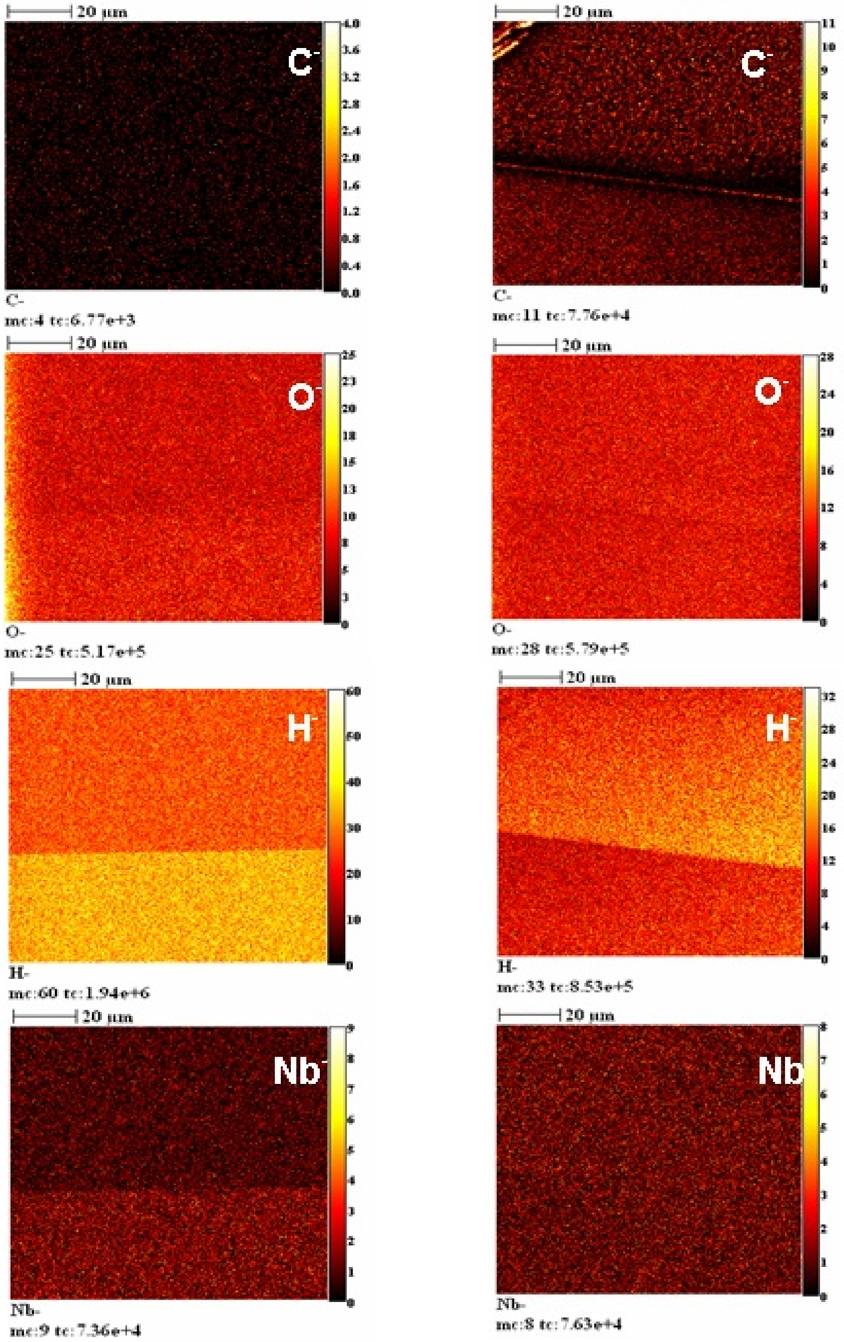

FIGURE 5: Grain boundary ion images of control (left column) and heat treated (right column) bicrystal samples.

CONCLUSION

Surface analysis of Nb bicrystals was performed using TEM , Dynamic SIMS and ToF SIMS. TEM showed a uniform grain boundary interface and a continuous oxide layer across the grain boundary. Dynamic SIMS and ToF SIMS measurements showed a difference in the H intensity within the same sample and in between the control and the heat treated Nb bicrystals. ToF- SIMS imaging depicted segregation of C on the grain boundary interface for the heat treated sample indicating that heat treatment process causes the C to diffuse into the grain boundary from the surrounding areas.

The difference in the ion intensities in the two crystals for both the samples could be attributed to the sputter rate differences caused by the differences in the crystallographic orientations. Further analysis for samples having similar orientations is thus needed.

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