

NANOSTRUCTURAL TEM/STEM STUDIES OF HOT AND COLD SPOTS IN SRF CAVITIES

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Abstract

Direct TEM/STEM imaging, down to subnanometer scale, and spectroscopic chemical characterization by EELS of the surface of mild baked/unbaked SRF cavity cutouts is implemented to correspond the changes in niobium surface to the SRF performance of the cavities. In situ cold stage observations reveal ordered hydride phases forming in the magnetic penetration depth of hot and cold spot cavity cutouts, which may help clarify the mechanism of the high field Q slope and its empirical cure.

INTRODUCTION

Experimental field dependence of the quality factors of superconducting radio-frequency (SRF) niobium cavities in the absence of well-known parasitic losses (multipacting, field emission, hydrogen Q disease) remains an important limitation in SRF cavity development. In particular, rapid drop of the quality factor (Q) observed above ≈ 100 mT, known as the high field Q slope (HFQS), restricts the performance and achievable accelerating gradients of SRF niobium cavities. HFQS in electropolished cavities can be cured by “mild baking” at 100-120°C in UHV for 24-48 hours, depending on grain size. The major reason for the HFQS is a strong increase of the residual resistance when surface RF magnetic field amplitude reaches a threshold around ≈ 100 mT. Understanding the causes of field-dependent rf losses, in particular HFQS, and the mechanism behind mild baking, will help improve existing cavity preparation, and enable future development.

Despite an extensive search for the material features within the penetration depth responsible for HFQS, a complete model of HFQS verified by experiments has not yet been established. It is important to recognize that the relevant length scale for the problem of HFQS and its cure by mild baking is limited to the first several tens of nanometers from niobium surface, as was recently confirmed by HF acid rinsing investigations [1]. It has been lately suggested that the HFQS may be due to nanoscale hydrides formation within this depth, and these nanoscale features may only be observed at cryogenic temperatures [2]. In the reported work we unambiguously confirm the existence of such nanoscale hydrides in the magnetic penetration depth of SRF cavities using direct TEM observations.

Our studies are based on comparison of samples that have been directly cut from 1.3 GHz SRF niobium cavities with and without HFQS. Thermometry during RF testing allowed us to select the representative “hot” spots in the

unbaked EP cavity, and representative “cold” spots in the 120°C baked EP cavity with no HFQS. Comparison of the cavity cutouts with different dissipation characteristics provides unambiguous grounds for the determination of HFQS causes and surface treatment effects.

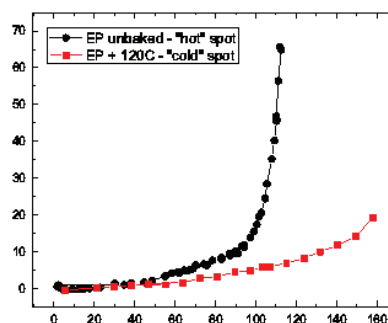


Figure 1: Temperature profile for hot and cold cavity cutouts.

We use Transmission Electron Microscopy (TEM) techniques, which are capable of adequate spatial and energy resolution, for direct structural and compositional characterization of cutout samples at the length scales of interest. Temperature dependent structural evaluation of the niobium near-surface region at temperatures down to 94 K has been studied, and nano-area electron diffraction (NED) has been used for structural characterization of the present phases. NED not only allows phase identification, like conventional selected area electron diffraction (SAD), but also provides a small interaction volume with the sample, allowing one to characterize nanometer-scale heterogeneous structures [3]. In comparison to all the other techniques only NED is capable of providing a direct check of the proposed nanohydride model with sufficient resolution. In this work we also use EELS for compositional comparison of oxidation states of the niobium surface in samples with different rf dissipation characteristics.

EXPERIMENTAL METHODS

Thermometry and TEM Sample Preparation

Based on temperature mapping data, two different types of cutouts have been used: “hot spot” cutouts, which show HFQS losses at high fields, and “cold spot” cutouts, which don’t show HFQS losses. For this study, a cold spot is a cutout taken from the fine grain electropolished cavity baked at 120°C for 48 hours as a final step of processing.

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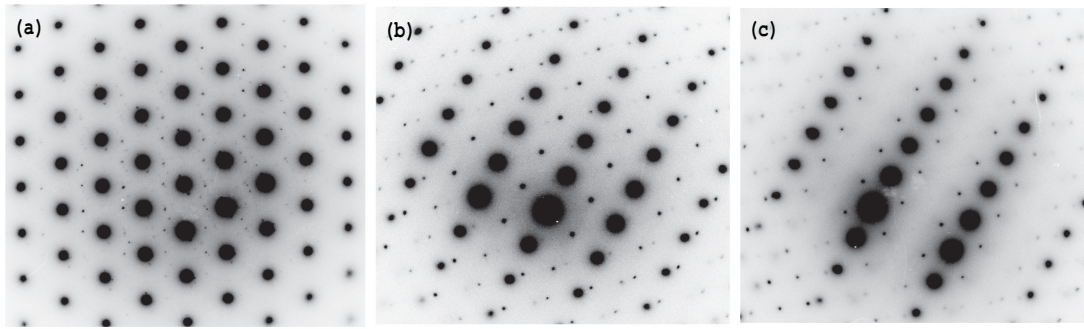


Figure 2: NED patterns taken from hot spot sample at 94K along different zone axes: (a) $[\bar{1}11]$, (b) $[113]$, (c) $[\bar{1}12]$.

Hot spot samples are taken from the cavity, which did not have *in situ* mild vacuum bake. Typical ΔT vs. B curves for the investigated samples obtained by thermometry are shown in figure 1.

In order to explore the near-surface layer of the cavity cutouts, cross sectional TEM samples were prepared by Focus Ion Beam (FIB) at a Helios 600 FEI instrument. Preservation of the native near-surface structure during preparation of TEM samples is crucial for our study. Therefore conventional polishing methods are not acceptable due to charging the sample with hydrogen [4]. FIB lift-out technique allows one to prepare and mount a small rectangular cross sectional sample onto a standard copper TEM half-grid using an Omniprobe micromanipulator. The top surface of each cross sectional cut was covered by a protective layer of platinum, in order to preserve the native niobium surface from Ga ions.

TEM Techniques

A JEOL JEM 2010F Schottky field-emission TEM, operated at 197kV and equipped with a post-column Gatan imaging filter (GIF), was used in this work for nano-area electron diffraction (NED) and electron energy loss spectroscopy (EELS). An approximately 70 nm sized NED parallel probe was used for NED. All diffraction patterns were recorded onto Fuji imaging plates and read by the a Fuji image plate scanner. A Gatan liquid nitrogen cooled double-tilt stage was used for the low temperature measurements. Energy dispersion was set to 0.3 eV/pixel for core-loss EELS niobium M-edge spectra.

RESULTS AND DISCUSSION

According to the proximity effect breakdown model of HFQS [2], differences in the precipitation state and quantity of niobium hydride complexes in the temperature region from 100 K to 150 K are keys to the drastically different rf losses between hot and cold spots. Within this model, the difference in precipitation state at low temperatures is caused by the mild bake. The absence of ordered niobium hydrogen complexes in hot and cold samples at room temperature is expected from the model and has been confirmed by room temperature NED measurements. Fig-

ure 2 and 3 demonstrate NED patterns taken at 94 K for the samples prepared from the hot and cold spot cutouts. Additional second phase(s) reflections are clearly observed along with niobium matrix. Formation of low temperature stoichiometric second phase(s) in the niobium-hydrogen system was previously detected by SAD for various hydrogen concentrations [5–7]. NED patterns were taken along the niobium-oxide interface of the FIB-prepared cross-sectional sample, corresponding to the magnetic penetration depth of the niobium SRF cavity. Diffraction patterns were taken sequentially by moving the parallel probe using the deflection coils. Three FIB prepared hot and three cold samples were investigated with NED. Comparing hot and cold spot samples, the number of probed spots exhibiting reflections of an additional low-temperature phase differ. For the hot spot samples, 44% to 68% of probed spots showed additional reflections. For the cold spot samples, 26% to 29% of the probed spots showed additional reflections. It has been also noticed that these additional low-temperature reflections vanish under exposure to the electron beam within a maximum time of 10 s. This can be explained in terms of the heating of the exposed area by electron bombardment, which allows hydrogen to regain its mobility and move to different parts of the sample. A similar effect was observed by Schober [5]. Due to this effect, relevant zone axis tilts were determined prior to cooling, and set up with no sample exposure at low temperatures. Exposure of the sample to the electron beam was minimized in order to preserve the native pattern of the second phase formation.

EELS spectra were taken in order to compare the oxidation state of the niobium surface before and after surface treatments, such as *in situ* mild bake and hydrofluoric acid rinsing. Figure 4 shows EELS spectra for niobium $M_{2,3}$ edge. EELS spectra were taken for four regions marked in the included high resolution TEM (HRTEM) image of niobium near surface (Figure 5). The approximately 5nm thick native niobium oxide is covered by a platinum protection layer deposited first by electron beam and then by ion beam. The $M_{2,3}$ edge of niobium is a result of the transition of Nb 3p electrons to unoccupied Nb 4d and 5s states [8]. Spin-orbit coupling of the 3p orbital causes the appearance

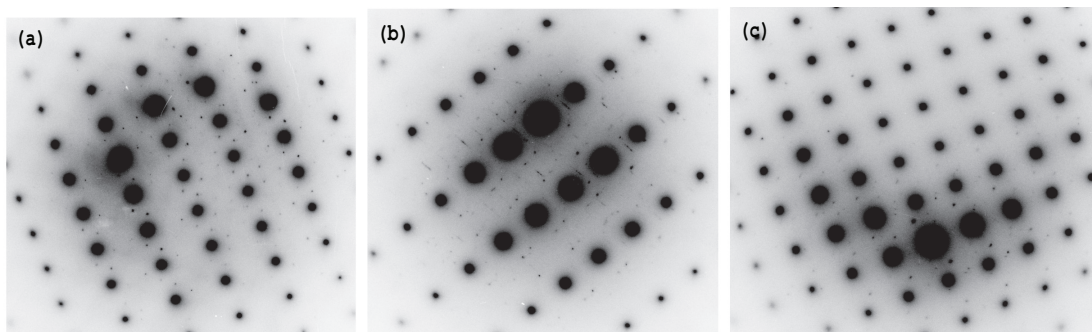


Figure 3: NED patterns taken from cold spot sample at 94K along different zone axes: (a) [011], (b) [113], (c) [001].

of two peaks (M_2 and M_3). Exposure time for each spectra was 10-12 s. All niobium core loss spectra were calibrated with respect to carbon K-edge onset at 286 eV using the second derivative method described in [9]. Three spectra for each region were added after the background subtraction (log-polynomial function was used for a background [10]) for the $M_{2,3}$ edge to increase signal-to-noise ratio. Thickness of the sample in the region of interest was estimated to be 41 nm.

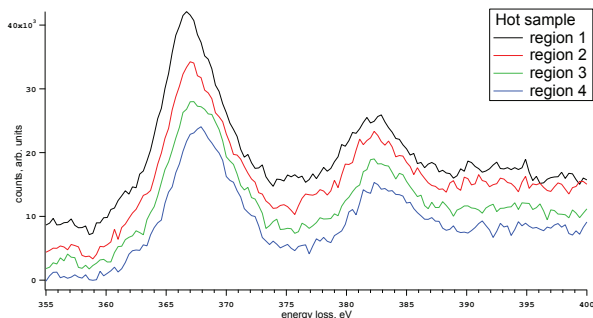


Figure 4: EELS spectra for hot sample.

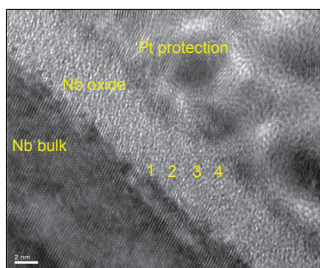


Figure 5: Regions for EELS spectra.

An approximately 1 eV shift of niobium M_3 peak between region 1 and region 4 is observed. A chemical shift of $M_{2,3}$ peaks toward higher energy suggests an increase in niobium valence/oxidation state [8]. The observed chemical shift, which is a function of distance from the metallic niobium surface, implies a change of oxidation state from 0 valence (metallic Nb) to valence ≈ 2.5 (Nb_2O_5) when mov-

ing away from metallic Nb. EELS Nb M-edge spectra will be collected from samples prepared from cold spots which have and have not been rinsed with hydrofluoric acid, in order to investigate possible changes of niobium surface oxidation with mild vacuum bake and HF-rinsing treatments.

CONCLUSIONS

We report preliminary transmission electron microscopy (TEM) results of nanostructural and compositional investigations of niobium SRF cavity cutouts with and without the high field Q slope losses. Formation of the second phase(s) in both kinds of samples has been directly observed by NED in the magnetic penetration depth upon in situ lowering of the temperature to 94 K. The difference between baked/unbaked samples has been observed in the volume fraction of the second phase. Such precipitation is in agreement with the proximity breakdown HFQS model and is attributed to the formation of niobium hydride based on its appearance at low temperatures. Phase characterization of low temperature second phase(s) crystalline complexes by electron diffraction indexing is ongoing. An additional electron diffraction experiment will be held in order to estimate the size of low temperature inclusions.

In progress is an EELS study of oxidation states of the near niobium surface of cavity cutouts subjected to different surface treatments (mild vacuum bake and HF-rinsing). $M_{2,3}$ niobium edge spectra taken from the surface region of a hot spot sample demonstrates an increase of niobium valence as a function of distance from metallic niobium surface. This is in the agreement with previous studies [8].

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