FAST TABLE TOP NIOBIUM HYDRIDE INVESTIGATIONS USING DIRECT IMAGING IN A CRYO-STAGE

F. Barkov, A.Romanenko*, A. Grassellino, Fermilab, Batavia, Il 60510, USA

Abstract

Precipitation of lossy non-superconducting niobium hydrides represents a known problem for high purity niobium in superconducting applications. Using cryogenic optical and laser confocal scanning microscopy we have directly observed surface precipitation and evolution of niobium hydrides in samples after different treatments used for superconducting RF cavities. The growth of hydrides is well described by the fast diffusion-controlled process with almost all hydrogen precipitated at $T = 140$ K within ~ 30 min. 120°C baking and mechanical deformation are found to affect hydride precipitation through their influence on the number of nucleation and trapping centers.

INTRODUCTION

Niobium can easily absorb hydrogen, which, depending on the concentration and temperature, may either stay as an interstitial or precipitate into ordered niobium hydride phases. A severe degradation of the superconducting radio frequency (SRF) cavities quality factor starting at very low accelerating fields - known as "hydrogen Q disease" - was attributed to formation of non-superconducting niobium hydrides [1].

More recently, smaller hydrides were proposed [2, 3] as a cause for another cavity limitation - a "high field Q slope", understanding of which is an area of active ongoing research.

Hydrogen can be absorbed by bulk niobium whenever natural oxide passivating layer is absent on the surface. There is a number of such opportunities during cavity fabrication and processing. It is therefore important to systematically investigate for cavity-grade niobium and surface treatments associated with cavities the details of how hydride form, their morphology, and effect of trapping centers. We present low-temperature studies performed by utilizing laser confocal and optical microscopy coupled with the cryogenic stage. These studies rely on the optical contrast and morphological changes for detection of hydrides and are focused on the particular surface treatments of relevance to SRF cavities.

EXPERIMENTAL METHODS

Square samples 15×15 mm^2 with 3 mm thickness were cut by wire electron discharge machining from fine ($\sim 50 \, \mu$m) grain and single grain RRR~ 300 niobium sheets

---

* aroman@fnal.gov

from the same material batches as were used to manufacture state-of-the-art performance cavities.

All the mechanical and chemical treatments have been performed in Fermilab using the in-house setups.

For cryogenic measurements samples were glued with Apiezon N grease to the cold finger of the optical cryostat. Liquid helium-based gas flow cryostat allowed to reach temperatures down to about 5 K. Real-time observations of niobium surface were done using a laser confocal optical microscope with a lateral resolution of the order of 1 μm in a temperature range 5-300 K. Lakeshore temperature controller was used to control and stabilize the temperature.

RESULTS

Hydrogen concentration in some of the samples we used has been measured by the gas chromatography technique at ATI Wah Chang with the results shown in Table 1. The technique does not allow to measure concentrations below ~ 3 weight ppm. Mechanical polishing (MP) led to the highest hydrogen concentration (24 to 71 weight ppm depending on the polishing duration), whereas electro-(EP) and buffered chemical polishing (BCP) under conditions similar to cavities did not affect hydrogen content.

Table 1: Hydrogen concentration (weight ppm) after different treatments as measured by gas chromatography.

Treatment	Single grain	Fine grain
no treatment	$10 \div 12$	< 3
120 μm EP	$11 \div 15$	<3
120 μm BCP	12	<3
MP	N/A	$24 \div 71$

Mechanically Polished Samples

Among the samples we studied, MP samples showed the highest hydrogen concentration. Hydride precipitation in these samples could not be avoided even with the fastest cool down (~ 10 minutes to 5 K). Thus MP samples provided an ideal system to investigate precipitation kinetics, morphology, effects of deformation, and of 120°C bake.

Precipitation kinetics Samples were quickly cooled down to 140 K and kept at this temperature for 3 hours while images of the hydride growth were taken (see Fig.1). It shows that hydrides grow very fast during first ~ 30 minutes after which the process becomes much slower but does not stop completely even after 3 hours.
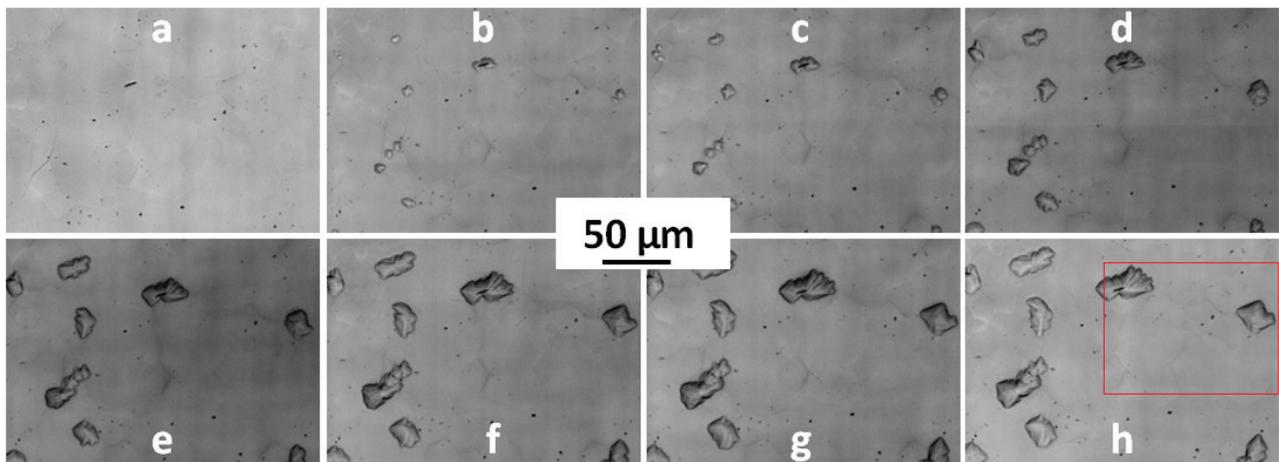
Figure 1: Time evolution of hydrides observed on a mechanically polished fine grain sample with $C_H = 25$ weight ppm at $T = 140$ K: a) room temperature; b) after 60 s at 140 K; c) 120 s; d) 300 s; e) 900 s; f) 2700 s; g) 6000 s; h) 10800 s.
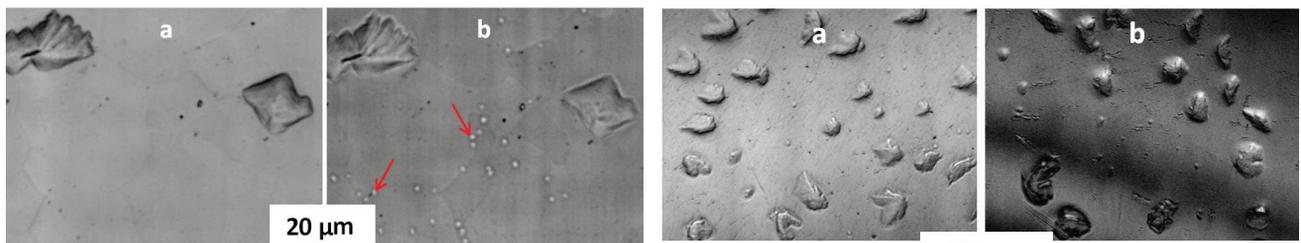

Figure 2: Enlarged view of the area in Fig. 1h: a) after keeping the sample for 3 hours at 140 K; b) after additional cooling to 5 K. Arrows indicate hydrides formed at 100 K.
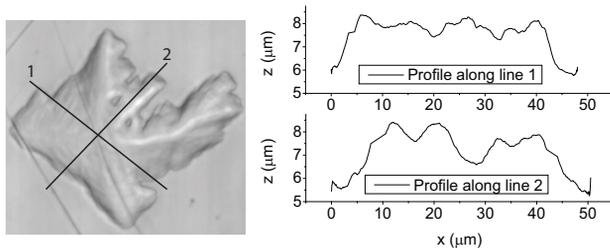
Figure 3: Typical profile of a hydride.

Figure 4: Patterns obtained after fast cooldown to 5K of mechanically polished fine grain samples with: a) no deformation, b) 7% tension, c) 10% tension, d) 12% tension

After a 3-hour hold at 140 K we rapidly ($\sim$20 K/min) cooled samples down to 5 K. As soon as the temperature reached ~ 100 K smaller in size hydrides appeared in the areas between the hydrides grown at 140 K [see Fig. 2]. They are formed preferentially at the grain boundaries. The same finding was confirmed on two other samples.

Hydride morphology Typical hydride profile obtained by LCSM at 160 K is shown in Fig. 3. All of the hydrides represented bumps on the surface with the characteristic height of about 3 μm. They appeared almost immediately and their height remained almost unchanged during further growth that was proceeding in the surface plane only.

Effect of deformation We prepared fine grain samples with the varying degree of tensile deformation. All the samples were then mechanically polished in the same batch to ensure the same hydrogen pickup. Hydrogen concentration measured by gas chromatography was 65$\pm$5 weight ppm in all the samples, thus the only difference was the degree of deformation. The results of fast cooldown tests are presented in Fig. 4. One can see a clear effect: higher deformation leads to a smaller number of hydrides.

Effect of 120°C bake We split several mechanical samples in two halves to preserve the same hydrogen content, and then baked one of the halves at 120°C in vacuum for 48 hours. While nucleation and evolution of hydrides at 140 K was found to be virtually unchanged, the behavior after further cooldown was found to be completely different - no small hydrides appeared upon cool down to 5 K.
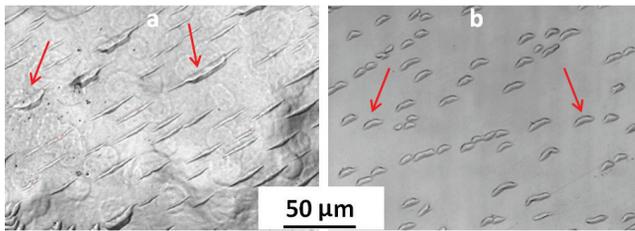
Figure 5: Hydrides formed during fast cooldown of single grain samples after 120 μm chemical material removal: a) EP, b) BCP. Arrows indicate hydrides

Precipitation after Standard Treatments

We put samples through a sequence of standard cavity processing steps and performed cryogenic tests after each treatment. Treatments included bulk material removal of 100-200 μm by EP or BCP, 800°C vacuum bake for 3 hours, "light" material removal of 20-40 μm, and a 120°C vacuum bake for 48 hours. The cooldown rate was chosen to be $\sim$ 10 K/min to "simulate" cavity conditions usually referred to as a "fast cavity cooldown".

First we studied fine grain samples and we did not observe any hydride formation in any of these experiments. In the case of single grain samples we observed the formation of hydrides in samples after bulk EP and BCP (see Fig. 5). Hydrides appeared at 140 K in the form of "lens-like" structures parallel to each other and grew along the longest dimension as temperature decreased down to $\sim$100 K. With further temperature decrease both dimensions and a number of hydrides remained constant. Upon warming up hydrides disappeared at a higher temperature of about 200 K and only dents similar to ones reported in [4] remained on the surface. After samples were baked at 800°C for 3 hours, no observable hydrides appeared during cooldown, and also none were found after subsequent treatments.

DISCUSSION

We have observed niobium hydrides by laser and optical microscopy at cryogenic temperatures. A strong correlation between the presence or absence of hydrides and the performance of similarly treated cavities suggests that large hydrides we observe are responsible for the "Q disease".

Among the standard treatments, only MP (analogous to tumbling) has led to the observable large hydrides in fine grain samples. This is in agreement with the fact that tumbled cavities have to be degassed at 600-800°C to avoid severe Q disease.

According to our results, 800°C baking for 3 hours is an effective way to preclude the formation of hydrides. This is in line with a well known fact that 800°C baking removes the Q disease [1].

Hydrides have a shape of islands, which punch out of the surface. In-plane dimensions depend on the concentration and the time spent in the precipitation temperature range. Height of hydrides is about 3 μm, much larger than the depth (150 nm) of the surface relief left by hydrides dissociation reported in [4].

Fig. 1 demonstrates that it takes only $\sim$30 minutes for the hydrides to reach almost maximal size. It means that even "fast cavity cooldown" will not help to avoid hydride formation when hydrogen concentration is high enough. From the absence of hydrides in any of 800°C baked samples we can only conclude that hydrogen concentration is not enough to form observable micrometer-size hydrides since our technique is limited in spatial resolution.

We think that slowdown of hydrides growth process can be attributed to a decrease of hydrogen supply from the bulk. In other words, after $\sim$30 minutes spent at 140 K most of the hydrogen is already segregated. Developing a model describing process of hydrides growth quantitatively is the subject of ongoing research.

We attribute the formation of smaller hydrides at 100 K to the precipitation of another hydride phase, which has a lower solubility limit. We speculate that this lower temperature phase may be responsible for the high field Q slope as suggested by the proximity-coupled hydride model [2]. 120°C baking suppresses the formation of this phase and there are different possible scenarios for the suppression - either the vacancies introduced by the 120°C bake trap some hydrogen [3], or 120°C baking leads to the removal of the hydride nucleation centers.

Higher deformation leads to the lower hydride density. Strong hydrogen attraction to dislocations is known to be responsible for the formation of Cottrell clouds with higher hydrogen concentration around dislocation cores in niobium [5]. In our case, dislocations created during plastic deformation can similarly trap some hydrogen.

CONCLUSIONS

We have developed a technique for direct observation of formation and evolution of niobium hydrides on the surface of cavity-grade niobium. We have investigated how different treatments used in cavities manufacturing affect the formation of hydrides through their influence on the concentration of dissolved hydrogen and on the number of trapping and nucleation centers. Our results correlate well with the performance of cavities after analogous treatments.

While segregation of most part of the hydrogen is a fast process with time constant $\sim$ 30 minutes, it takes much more time > 3 hours to collect all the hydrogen.

ACKNOWLEDGMENT

REFERENCES

[1] B. Bonin and R. W. Roth, "Proceedings of the 5th Workshop on RF Superconductivity", SRF 1991, Hamburg, August 1991, p. 210, http://www.JACoW.org

[2] A. Romanenko et al, Supercond. Sci. Tech. 26 (2013) 035003.

[3] A. Romanenko et al, Appl. Phys. Lett. 102 (2013) 232601.

[4] F. Barkov et al, Phys. Rev. ST Accel. Beams 15 (2012) 122001.

[5] J. A. Rodriguez and R. Kirchheim, Scripta Metallurgica 17 (1983) 159.