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Direct observation of hydrides formation in cavity-grade niobium

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Abstract

Niobium is an important technological superconductor used to make radio frequency cavities for particle accelerators. Using laser confocal microscopy we have directly investigated hydride precipitates formation in cavity-grade niobium at 77 and 140 K. We have found that large hydrides were usually formed after chemical or mechanical treatments, which are known to lead to a strong degradation of the quality factor known as Q-disease. From our experiments we can conclude that hydrides causing Q-disease are islands with a characteristic thickness of $\sim$ 100 nm and in-plane dimensions 1-10 μm. Our results show that mechanical polishing uploads a lot of hydrogen into bulk niobium while electropolishing leads to a mild contamination. Vacuum treatments at 600-800°C are demonstrated to preclude large hydride formation in line with the absence of Q-disease in similarly treated cavities.

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I. INTRODUCTION

The phenomenon of drastic drop of niobium superconducting radio frequency (SRF) cavities quality factor Q_0 at low accelerating fields below 2 MV/m without field emission or multipacting was encountered more than 20 years ago [1–4]. It was found that a fast cool-down ($<$ 1 hour from room temperature to 4.2 K) could in some cases solve the problem. A conclusion was made that the precipitation of the dissolved hydrogen as lossy hydrides at the RF surface at temperatures 100-150 K was the reason for the increase of the surface resistance. These hydrides are normal conducting at cavities operating temperature of about 2 K. The effect was named "hydrogen Q-disease". It was supposed that the extent of Q-degradation depends on the quantity of dissolved hydrogen, the cool-down rate, and the amount of atomic size defects and interstitial impurities serving as nucleation centers for forming hydrides [3–6]. Degassing in a vacuum of better than 10^{-6} Torr at 800°C for 2-3 hours or at 600°C for 10 hours cures hydrogen contamination, restores low resistance state and removes Q-disease [1, 7].

Typical niobium cavity fabrication procedure consists of multiple steps, which include half-cell stamping, weld preparation, light etch and electron beam welding of the half-cell cups and beam tubes together. Manufactured cavities are then put through a sequence of different treatments developed primarily by empirical methods. Typically, bulk chemical removal by buffered chemical polishing (BCP), electropolishing (EP) or, more recently, centrifugal barrel polishing, are applied to remove $\gtrsim 120\ \mu$m from the surface. In the current processing sequence for ILC it is followed by 800°C vacuum bake for 2 hours, light EP ($\sim 20\ \mu$m), high pressure water rinsing (HPR), and 120°C in situ bake for 48 hours.

In general, whenever natural oxide layer is not present on the surface of niobium, there is a possibility for hydrogen pick up. Such opportunities for hydrogen to enter niobium exist along the processing steps. Chemical polishing (EP or BCP) is suggested to be one of the pathways whereby niobium becomes contaminated with hydrogen [8]. In the case of BCP it was found that keeping the acid temperature below 15°C helped minimizing hydrogen upload [9]. Mechanical polishing using a solution, which is not hydrogen-free, generally results in a strong hydrogen contamination [10]. Finally, reabsorption from the furnace upon cooldown is another possible hydrogen pick-up route [7, 11, 12].

Nb-H systems were studied extensively in 1970s [13–15]. A complete equilibrium phase

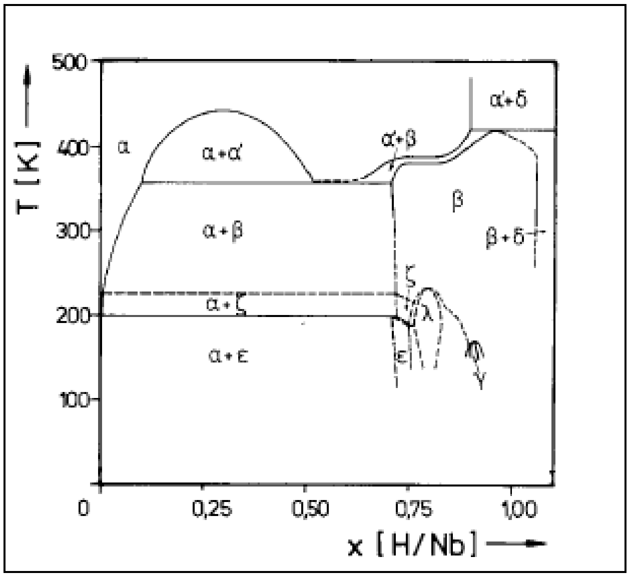

FIG. 1. Phase diagram of Nb-H system (from Ref. 15).

diagram is presented in Fig. 1. Niobium can dissolve large amounts of hydrogen on interstitial states. The α-phase is the solid solution in which hydrogen atoms are distributed on random tetrahedral sites. At room temperature the solubility limit of this phase extends up to 4 atomic % of hydrogen. But this limit is drastically reduced with temperature decrease and is about 5×10^{-4} atomic % at 100 K. When hydrogen concentration is above the solubility limit, different stoichiometric hydrides can be formed.

Despite the fact that the formation of hydrides is considered to be a well-established reason for the Q-disease they were never observed in cavities or cavity-grade material so far with only hypotheses put forward regarding their size, shape and distribution [6]. This motivated us to carry out presented metallographic studies of SRF cavity-grade niobium samples. We have tried to investigate by direct observations how different treatments used for cavity processing affect the formation of hydrides.

II. EXPERIMENTAL

Our samples were cut by wire electron discharge machining (EDM) from fine grain and large grain RRR $\gtrsim 300$ niobium sheets from the same material batch as was used to manufacture 9-cell and 1-cell cavities with the state-of-the-art performance. Samples were embedded in either Bakelite or epoxy pucks and mechanically polished first by the increasing grit size

(120-600) sandpaper. It was followed by the automated polishing on the Textmet polishing cloth with 6 μm size diamond solution for several hours. Final polishing was done on the vibrational polishing machine with the colloidal water-based SiC solution. Electropolishing (EP) was performed using the in-house sample electropolishing setup with the standard acid solution used for cavities. 800° baking was accomplished in the same vacuum furnace, which is used for cavities. 120° baking was done using a continuously pumped vacuum tube with resistive heating on the outside walls.

To study hydrides formation we either immersed the samples in liquid nitrogen or when a temperature above 77 K was needed we kept the samples in a nitrogen vapor above liquid level. The farther away from the liquid the higher the equilibrium sample temperature was. By adjusting the distance between a sample and liquid nitrogen level it was possible to stabilize temperature within 10 K range. After warming the samples up to the room temperature we used a laser confocal optical microscope with a lateral resolution of order 1 μm to observe obtained surface structures.

III. RESULTS

First we studied mechanically polished samples without any subsequent chemical treatment. Presented in Fig. 2 is a typical pattern obtained on a fine grain sample after placing it into liquid nitrogen for 1 hour. Lens-like structures of a characteristic size of about 1-3 μm are clearly seen. No such structures were observed before placing the sample into liquid nitrogen. There is no difference between the patterns obtained after 1 hour and after keeping samples in liquid nitrogen for 24 and 48 hours.

Then we looked at the samples after mechanical polishing, 800°C baking for 2 hours and keeping in liquid nitrogen for 24 hours. No apparent structures were observed. It is in a good agreement with a commonly accepted concept that 800°C baking reduces bulk hydrogen concentration significantly which prevents the formation of large hydrides upon cooldown.

To investigate the possible 120°C baking effect we polished one of the samples mechanically and baked it at 120°C for 48 hours before putting the sample into liquid nitrogen. The surface structures obtained are similar to those without 120°C treatment.

To check if the surface structures we observed are purely morphological or represent room-

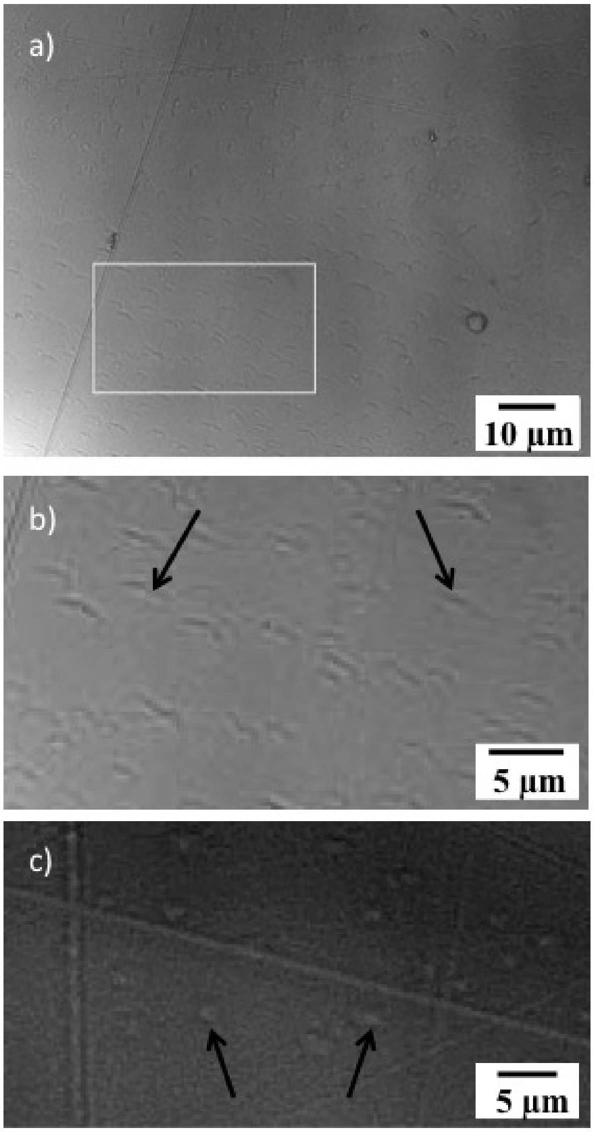

FIG. 2. a) Lens-like structures after 77 K hold on a fine grain mechanically polished sample; b) zoom-in from the selected area, arrows indicate surface relief due to hydrides; c) smaller structures observed at another location.

temperature hydrides, we baked one of the samples at 800°C for 2 hours after structures had been already formed. Structures did not disappear, and our interpretation of this fact consists in the following. Lattice constant in a hydride phase is about 10 % larger than in pure niobium. When sufficiently large hydrides are formed it leads inevitably to the mechanical deformation of the crystal around the precipitate. And it is this surface relief (not hydrides themselves) that we observe in a microscope. It explains why we can observe structures at room temperature where hydrides must have already disappeared according to

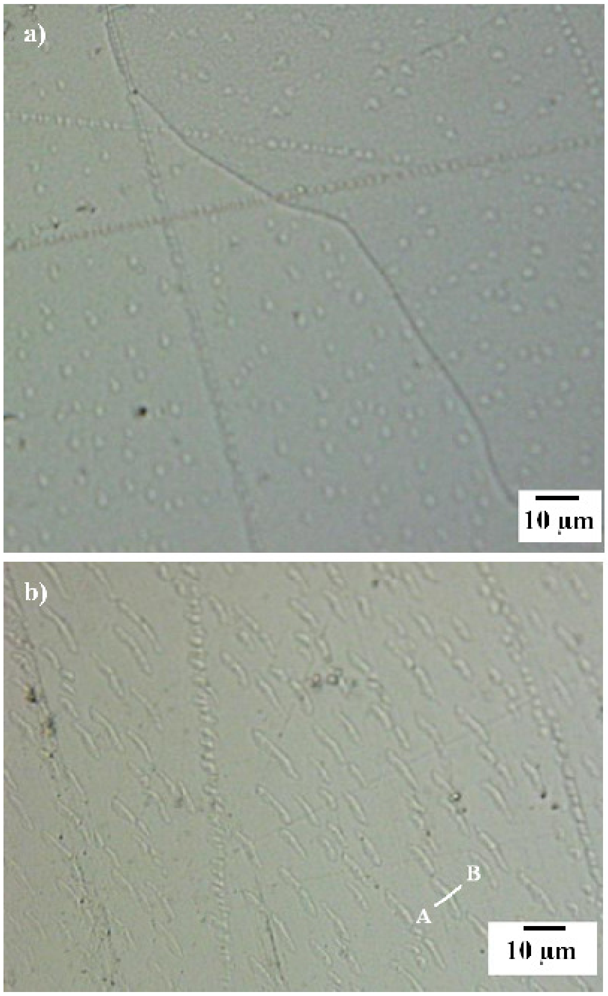

FIG. 3. Lens-like structures after 77 K hold on mechanically polished a) fine grain sample; b) single grain sample.

the phase diagram, and why these structures remain after 800°C bake.

It is interesting to mention that hydride relief structures in adjacent grains are oriented in different ways suggesting that their alignment is affected by crystallography. In line with this, a pattern obtained on the single grain sample (see Fig. 3) shows lens-like structures parallel to each other.

Another apparent feature is that hydrides decorate surface irregularities like scratches. This may mean that hydrogen is segregated at the irregularities before the cooldown or that such features provide nucleation centers for the hydride to form or both.

Fig. 4 shows a typical surface profile across the groove due to large hydride formation. Characteristic height difference is of the order of 100 nm.

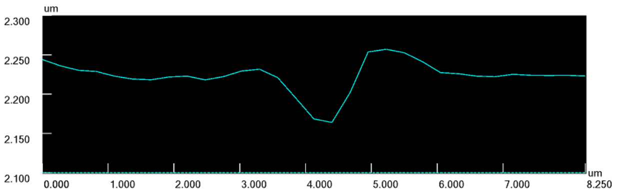

FIG. 4. Surface profile across the AB line from Fig. 3

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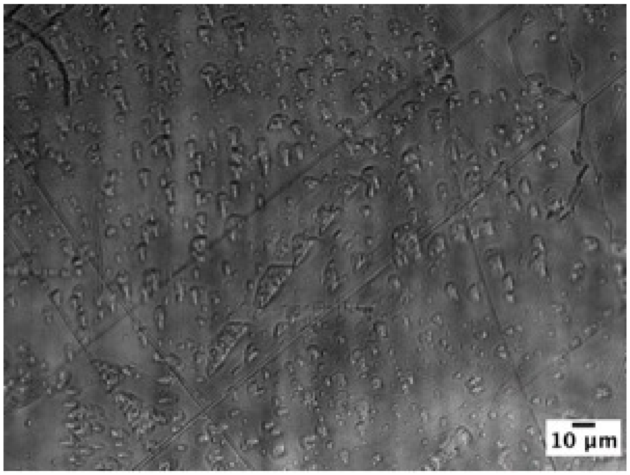

FIG. 5. Patterns obtained after keeping mechanically polished sample at 140 K for 1 hour.

We produced analogous experiments at a higher temperature of 140 K by keeping samples in nitrogen vapor as described above. Fig. 5 shows much larger structures of a characteristic size of 10 μm formed under these conditions. Some of them even have different “star-like” shape.

One of the important questions in cavities manufacturing is if and when chemical treatments lead to additional hydrogen upload. This is especially important since light electropolishing to remove 20-40 μm of the material is customary at many labs after 600-800°C hydrogen degassing. We took 800°C baked sample and removed a 40 μm layer by electropolishing. After keeping the sample in liquid nitrogen we did not observe any structures. But after keeping the sample at 140 K some microscale structures appeared. Fig. 6 shows the evolution of hydrides formation with time. There was no apparent growth of the hydrides over three different times of observation. This may mean that precipitation reached the saturation determined by hydrogen availability and one can make a conclusion that 40 μm electropolishing does upload some hydrogen but not as much as the mechanical polishing.

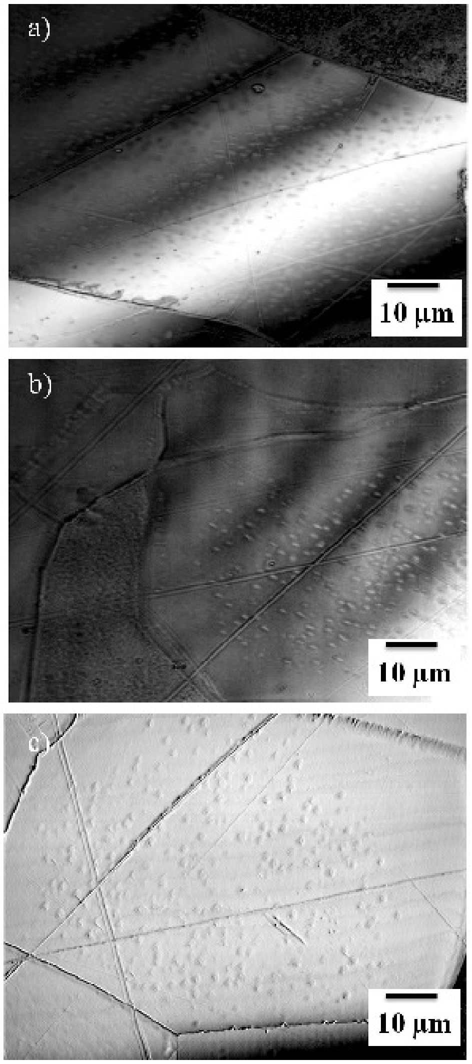

FIG. 6. Patterns obtained after keeping electropolished sample at 140 K for a) 1; b) 2; c) 4 hours.

IV. DISCUSSION

Hydrogen atoms are extremely mobile in niobium. Coefficient of diffusivity is $D \sim 10^{-5}$ cm^2/sec at room temperature and decreases exponentially at lower temperatures. That is why even when hydrogen concentration is above solubility limit for a particular temperature, some nucleation centers are necessary to trap hydrogen atoms to form hydrides. Such centers can be vacancies or other point defects. Resulting hydride size after a particular cooldown process depends on the amount of trapped hydrogen which, in turn, is proportional to hydrogen concentration and to a volume $(\sqrt{Dt})^3$ from which hydrogen can diffuse towards a nucleation center. There are two different possibilities for hydrides to stop grow-

TABLE I. Effect of different treatments.

Treatment	77-140 K hold outcome	Typical cavity performance
Mechanical polish (MP)	Large hydrides	Q-disease
+800C 3 hrs	No hydrides seen	No Q-disease
+BCP 5 min	No hydrides seen	No Q-disease
+120C 48 hrs	No hydrides seen	No Q-disease
MP + 800C 3hrs + EP 40 min	Small hydrides after 140K	No Q-disease

ing. The first one is when $\sqrt{Dt}$ becomes comparable with the distance between adjacent nucleation centers, all hydrogen becomes segregated and hydrides stop growing due to the lack of hydrogen supply. Another one can be realized due to the lack of hydrogen mobility when the temperature becomes low. In this case hydrogen distribution remains "frozen" with the size of hydrides determined by the time spent at higher temperatures. We believe in our experiments we have encountered both of these growth stopping scenarios.

In particular, in cases of 77 K and 140 K hold of similarly treated samples there is no difference among pictures obtained after keeping samples for different durations at these temperatures. At the same time there is a significant difference in sizes of hydrides obtained at 140 (Fig. 5) and 77 K (Fig. 2). Therefore there is more hydrogen available for segregation at 77 K but hydrides are not growing. A logical interpretation of this fact could be lack of hydrogen mobility. Similarly, 140 K result appears to be determined by hydrogen supply. Hence one can make a conclusion that only when we are passing 100-150 K interval in a process of cooling down hydrides are really growing.

Based on the above, surface relief picture obtained after 77 K holds can mimic the distribution of large hydrides, which is realized in niobium cavities upon "fast" cooldown typical of cavity operations. Similarly, 140 K hold can be used as a representative for "slow" cooldown. Summary of our findings for different treatments is shown in Table I. We observe a strong correlation between our findings and cavity performance after the same treatments.

It should be noted that since our experimental technique relies on the formation of surface relief we can not exclude the presence of hydrides at cryogenic temperatures in the samples where we found no surface relief after cryohold. Lateral resolution of our microscope is limited to about 1 μm and hence smaller hydrides could have been present during the hold leaving surface relief which is beyond the resolution available to us. There may also in principle exist hydride phases, which do not leave a signature surface relief at all, for example due to the smaller mismatch between the lattice parameters with host niobium. Therefore our observations can only provide “lower bound” on the hydride precipitation after a particular surface treatment.

V. CONCLUSIONS

We have developed a procedure and directly observed surface relief caused by the formation of niobium hydrides on the surface of the cavity-grade material. We correlated the formation of hydrides with the Q-disease observed in SRF niobium cavities and explicitly described the morphology and characteristic sizes of culprit hydrides.

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