DIRECT OBSERVATION OF HYDRIDES FORMATION OF NITROGEN DOPING Nb SAMPLES*

Z. Q. Yang, X. Y. Lu, W. W. Tan, D. Y. Yang, Y. J. Yang, J. F. Zhao
State Key Laboratory of Nuclear Physics and Technology, Peking University, Beijing, China

Abstract

Direct observation of hydrides precipitates formation on both nitrogen doped and un-doped Nb samples at 80K has been carried out using Scanning Electron Microscope (SEM) with Cold Stand. We have found that, under our experimental conditions, when the subsequent EP removal is less than 7µm, the amounts of hydrides formed on the surface of doped samples can be effectively reduced. When the subsequent material removal is larger than 9µm, the amounts of precipitated hydrides increased with the EP removal. When the EP removal is 7-9µm, the amounts of hydrides can still be effectively reduced. Also, more hydrides were precipitated on the surface of un-doped samples. The amounts of hydrides of doped samples may be reduced to varying degrees with different amounts of material removal.

INTRODUCTION

The niobium hydrides are normal conducting at the typical cavity operating temperature of about 2K. Both previous and present studies have shown that the amounts of lossy non-superconducting niobium hydrides precipitated on the inner surface of the superconducting radio frequency (SRF) cavity have a significant influence on the Q value of the cavity. So hydride is an important source of residual resistance in the SRF niobium cavity. Therefore, special attention is needed to be paid to the changes of the precipitate of niobium hydrides on the surface of niobium samples before and after nitrogen doping treatment.

Nb-H systems have been widely studied in the 1970s for hydrogen storage as niobium figures among metals able to accept and restitute a large volume of hydrogen even at room temperature [1-3]. A complete equilibrium phase diagram is presented in Fig. 1. At room temperature, H atoms randomly distributed over tetrahedral sites in the crystal lattice. This is the α phase. The solubility limit of this phase extends up to 4 atomic percent of hydrogen at room temperature, which corresponds to more than 4×10^3 wt ppm of H concentration. So niobium hydrides do not form on the surface of RRR~300 high purity niobium, of which the H concentration is less than 2 wt ppm. As the temperature is lowered, the hydrogen concentration needed to form the hydride phases decreases. At 100K, solubility limit of the ε phase hydride is dramatically reduced to about 5 wt ppm. A well-known phenomenon about H in metals is its tendency to interact with crystal defects like impurity atoms, grain boundaries, and dislocations due to elastic stresses applied to the lattice. H keeps con-

centrated near the defect and can even reach niobium hydride precipitation limit, resulting in the formation of different stoichiometric hydrides. The diffusion rate of hydrogen between 150 K and 60 K remains quite significant, so that hydrogen can move to accumulate to critical concentrations at nucleation sites. When the temperature is reduced to below 60 K, the diffusion of hydrogen was slowed down so that hydrogen can no longer accumulate to the hydride centers.
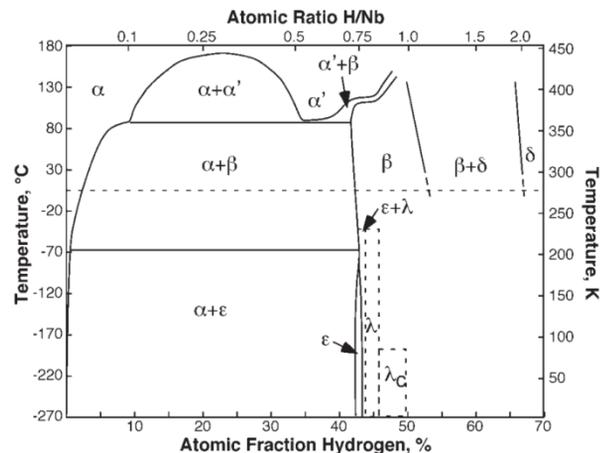

Figure 1: Phase diagram of Nb-H system [3].

To observe the hydrides precipitates formation on the surface of niobium, the niobium sample should be kept in a low temperature environment between 150 K and 60 K. Two methods have been used to the observation of niobium hydrides precipitation. One is the scanning transmission electron microscopy (STEM) [4]. Combined with the electron energy loss spectroscopy (EELS), the atomic scale structure information of niobium hydride can be observed. The other is the cryogenic laser scanning confocal microscopy (CLSCM) with a lateral resolution of the order of 1 µm in a temperature range 5-300 K [5]. The effect of different post treatments on the formation of hydrides on niobium surface at low temperature can be observed on the micron scale. Taking into account our experimental conditions and experimental requirements, the observation of hydrides precipitates formation on both nitrogen doped and un-doped Nb samples was carried out by using the scanning electron microscope (SEM) with a cold stand at 80K.

EXPERIMENTAL PROCEDURES

Sample Preparation

The sample preparation, nitrogen doping treatment and 800^0C heat treatment of the niobium samples can be seen in [6].

Observation of Hydrides Precipitation

Before the experiment, the samples to be observed was adhered to the centre disk area on the sample holder by conductive silver adhesives. The area around the disc is surrounded by metallic copper to increase the thermal conductivity, and the sample can be cooled better. After the sample holder was carefully fixed on the cold stand, the stand can be cooled by the cold nitrogen gas that has been cooled by liquid nitrogen.

Before the cooling of the sample, a number of observation points are selected randomly and their position coordinates are recorded on each sample in order to realize the switching between different samples in the observation process, and to compare the changes of the surface shape of each sample before and after cooling. During the process of experiment, a pressure of better than 1×10^{-4}Torr is obtained in the analysis chamber and the electron gun is in a high vacuum of about 10^{-9}-10^{-10}Torr. The electron beam current is about 326μA, the accelerating voltage is 10keV and the working distance is about 10.5cm. The sample temperature was reduced from room temperature to 80K within 10 minutes and remained unchanged at 80K.

Both doped and un-doped samples from two groups were chosen for the XPS experiments. That is ND-2nd-0μm, ND-2nd-7μm, ND-2nd-17μm, ND-2nd-21μm, HT-2nd-20μm and noNDnoHT. The labels begin with ND (HT), followed by a serial number and ended by a exact number means a doped (800^0C heat treated) sample from group 1 or group 2 with a certain amount of EP removal. The label noNDnoHT means the sample directly after EP removal of 150μm without nitrogen doping treatment or 800^0C degasing treatment.

RESULTS

Verification of Niobium Hydrides

The surface morphology changes of the noNDnoHT sample with temperature at the same observation position are shown in Fig. 2. It can be seen that the observed white island bumps precipitated at 80K disappeared when the sample temperature was raised up to 206K. Combined with the literature and Nb-H phase diagram, it can be judged that the observed white island bumps are precipitated niobium hydrides.
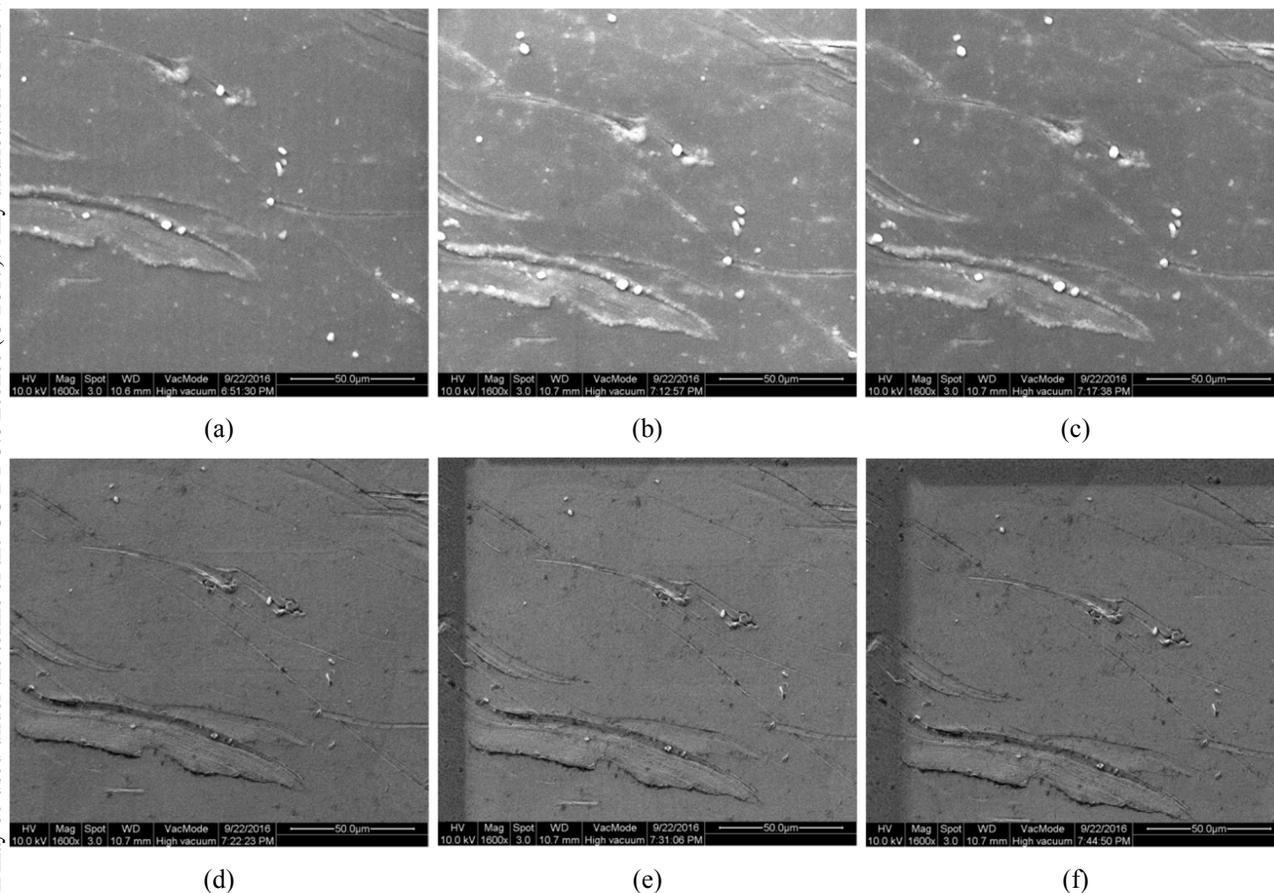

Figure 2: At the same observation position, the surface morphology of the noNDnoHT sample changes with the temperature: (a) 80K, (b) 190K, (c) 198K, (d) 206K, (e) 250K, (f) 298K.

Hydrides Precipitation of Samples with Different Treatments

Comparison of the specific precipitation of niobium hydrides at a random observation position in each sample is shown in Fig. 3. Observations showed that as soon as the sample temperature was reduced to 80K, obvious hydrides have been precipitated on the surface of the noNDnoHT sample. When the noNDnoHT sample was maintained at 50K for 50 minutes, the size and amounts of hydrides do not change substantially over time.
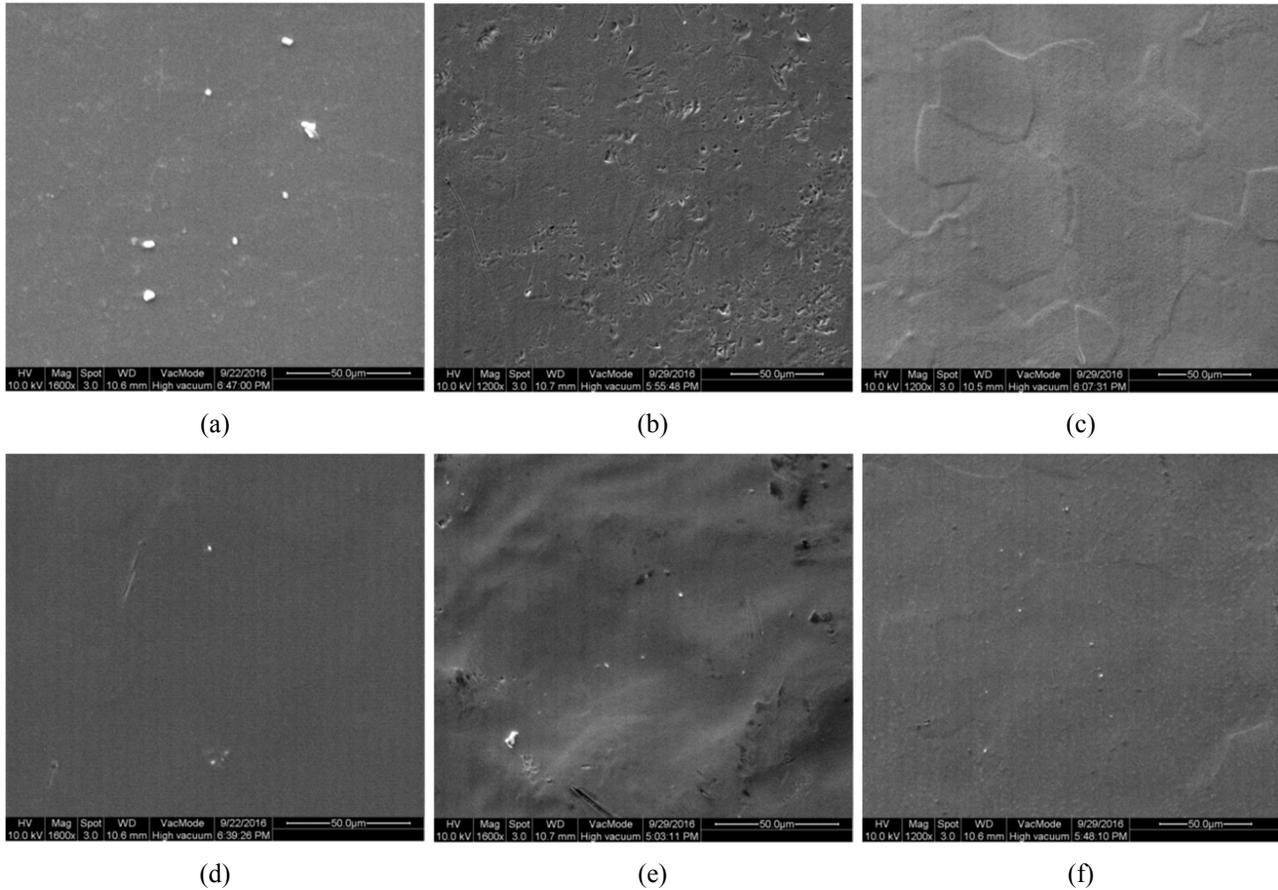

Figure 3: Comparison of the specific precipitation of niobium hydrides at a random observation position in each sample.

The largest number of niobium hydrides was precipitated on the surface of the noNDnoHT sample. The characteristic size of the island bump shaped hydrides on the surface of the noNDnoHT sample is about $3\mu m \times 3\mu m$. The HT-2nd-20μm sample, which undergoes 800^0C heat treatment and a subsequent EP removal of 20μm, showed a significant different formation of hydrides than that of the noNDnoHT sample. There is also a considerable amount of hydride precipitated on the surface of the HT-2nd-20μm sample, but the size of the hydrides is noticeably smaller than that of the noNDnoHT sample. This implies that the H content in niobium can be effectively reduced by 800^0C heat treatment and therefore to prevent Q disease.

No niobium hydrides were observed at any observation position on the surface of both ND-2nd-0μm sample and ND-2nd-7μm sample. However, niobium hydrides begin to precipitate on the surface of ND-2nd-17μm sample again, when the subsequent EP material removal reached 17μm under our experimental conditions. The amounts of niobium hydrides precipitated on the surface of ND-2nd-21μm sample with the sustained reduction of N concentration. The characteristic size of the hydrides precipitated on the surface of ND-2nd-17μm sample and ND-2nd-21μm sample is comparable with that of the HT-2nd-20μm sample. But the amounts of niobium hydrides precipitates did not recover to that of the HT-2nd-20μm sample, which means that the nitrogen doping effect of depth exceeds 21μm under our doping recipe. The observations also showed that the amounts of hydrides precipitation can be prevented or retarded to varying degrees with different amounts of material removal, which corresponds to the varying concentrations of doped nitrogen.

DISCUSSION

The amounts of lossy non-superconducting niobium hydrides precipitated on the inner surface of the superconducting radio frequency (SRF) cavity have a significant influence on the Q value of the cavity. A hypothesis that N-H interaction may be the physical mechanism for

proper nitrogen doping treatment to obtain high quality factor is proposed. Previous studies showed that N impurity in interstitial form can reduce the hydrogen diffusion coefficient in niobium at low temperatures by both quasielastic neutron scattering method [7] and Gorsky-effect measurements method [8]. Combined with the XPS study [9] and MPMS study [10], a possible mechanism concerning nitrogen doping phenomenon was proposed based on the N-H interaction. The average number of hydrides in all observation positions on each nitrogen doping sample surface, together with the Ginzburg-Landau parameter κ of nitrogen doping samples with different subsequent EP removal is shown in Fig. 4.
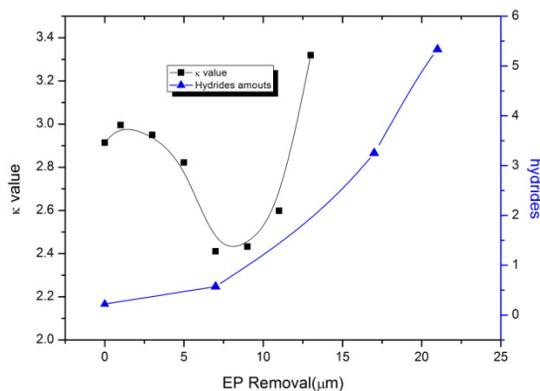

Figure 4: The average number of hydrides in all observation positions on each nitrogen doping sample surface, together with the Ginzburg-Landau parameter κ of nitrogen doping samples with different subsequent EP removal.

For the cavity directly after nitrogen doping treatment, the high concentration of nitrogen impurity at the surface layer of the doped sample can provide large amounts of flux pinning centres, possibly resulting in high residual resistance. The unloaded Q can be as low as the order of 10^7. When the EP removal is less than the optimized value, although the amounts of hydrides may be effectively lowered due to the reduction of hydrogen diffusion coefficient, the relatively high concentration of point defects from diffused nitrogen will trap more flux. And the residual resistance is still not small enough. When the EP removal reaches the optimized value, the point defects concentration in the surface layer is reduced remarkably. The interaction between hydrogen and nitrogen will either prevent hydrogen in the bulk niobium diffusing to the surface layer or retards the accumulation of hydrogen to critical concentrations at nucleation sites during the dangerous cooling section of 150-60K, so that the amounts of hydrides can still be effectively reduced. In this way, the total residual resistance will be a minimum and the Q_0 is largest. When the EP removal is larger than the optimized value, the hydrides can no longer be effectively reduced. More hydrides precipitates will emerge with the increase

of EP removal. Then there will be the recovery Q-slope. Under the condition of nitrogen doping treatment in our experiment, the optimized value of EP removal is considered to be 7-9μm.

CONCLUSION

Direct observation of hydrides precipitates formation on both nitrogen doped and un-doped Nb samples at 80K has been carried out using Scanning Electron Microscope (SEM) with Cold Stand. The amounts of hydrides of doped samples were reduced to varying degrees with different amounts of material removal, which corresponds to the varying concentrations of doped nitrogen. Under our experimental condition, the doped sample with subsequent material removal of 7-9μm corresponds to the minimum nitrogen concentration that can effectively reduce the amounts of hydrides formation. Combined with the XPS study and MPMS study, a possible physical mechanism of nitrogen doping phenomenon based on the N-H interaction is proposed.

ACKNOWLEDGEMENT

REFERENCES

[1] T. Schober, *Scr. Metall.* **7**, 1119 (1973).

[2] H. K. Birnbaum, M. L. Grossbeck, and M. Amano, *J. Less-Common Met.* **49**, 357 (1976).

[3] J.-M. Welter and F. J. Johnen, *Z. Phys. B* **27**, 227 (1977).

[4] Y. J. Kim, R. Tao, R. F. Klie and D. N. Seidman, *ACS nano*, **7** 732 (2012).

[5] F. Barkov, A. Romanenko and A. Grassellino, *Phys. Rev. Spec. Top-AC.* **15**, 122001 (2012).

[6] Z. Q. Yang *et al*., "TOF-SIMS study of nitrogen doping Niobium samples", Proceedings of SRF, Whistler, Canada, 2015, pp. 169-173.

[7] D. Richter, J. Topler and T Springer, *J. Phys. F: Metal Phys*. **6** L93-L97 (1976).

[8] Z. Qi, J. Volkl, H. Wipf and G. Alefeld, *Journal de Physique* **42** 763-768 (1981).

[9] Z. Q. Yang *et al*., "XPS Studies of Nitrogen Doping Nb Samples before and after GCIB Etching", SRF2017, Lanzhou, China, July 2017, paper THPB029, this conference.

[10] Z. Q. Yang *et al*., "Magnetic Properties of Nitrogen Doping Nb Samples", SRF2017, Lanzhou, China, July 2017, paper THPB031, this conference.