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MICROSTRUCTURE CHANGES OBSERVED IN THE NEAR-SURFACE REGION OF SRF Nb CAVITIES CUTOUTS UPON COOLING/HEATING CYCLES USING GI-SYNCHROTRON XRD

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Abstract

This contribution discusses the results of a structural study of the near-surface region from GIXRD data on cutouts from cavities treated with RF state-of-the-art surface treatments such as: N-doping, low-T bake (75/120C), and standard-T EP. For N-doping, the main phase found was Nb(NH_x) solid solution where the N atoms occupy the interstitial octahedral sites of Nb, trapping hydrogen atoms located in the tetrahedral sites. This avoids the formation of Nb-hydrides upon cooling. A similar effect appeared with the existence of oxygen as an absorbed species in Nb, particularly in the low-T baking cutout. Interestingly, the Nb-hydride formation on the sample cooling was detected only for the standard T-EP cutout, which is related with an ordered solid solution of Nb, α-Nb(H). The recorded GIXRD patterns provided a conclusive clue on such phase composition.

INTRODUCTION

Niobium is the metal superconductor of choice for SRF cavity technology because of its high surface superconducting properties and formability, which facilitates the cavities manufacture. Nb is a highly reactive metal, particularly for hydrogen, nitrogen, oxygen, and carbon, and these elements can be found in the near-surface region forming hydrides, nitrides, oxides, carbides, or forming solid solutions. That region is relevant for the cavity's performance because the superconducting current flows through a thin surface layer, of about 100 nm thick, and from this fact, the presence of structural defects, secondary phases, species dissolved the Nb structure, etc. could have a detrimental effect on their functional properties. During the manufacture, the cavity is submitted to several thermal and chemical surface treatments which remove the oxide layer, mainly formed by Nb_2O_5/NbO. The oxide layer passivates the surface and behaves as a barrier for hydrogen absorption. When it is removed, the naked Nb surface facilitates the uptake of hydrogen, which is finally found occupying the tetrahedral and octahedral interstitial sites in the Nb bcc unit and precipitates as hydrides upon cooling. These niobium hydride precipitates have a detrimental effect on the cavity quality factor, Q_0, known as High Field Q-Slope, due to proximity effect by normal conducting state of Nb-hydrides. This study reports a phase analysis for the near-surface region on cutouts from cavities treated with RF state-of-the-art surface treatments such as: N-doping, low-T baking (75/120C), and standard-T EP as function of cryogenic cooling and warming cycle. The results herein discuss the mechanism by which N and O as dissolved species in the Nb matrix minimize the detrimental effect of hydrogen in the cavity performance.

EXPERIMENTAL

The cutouts herein studied were obtained from the cavity after the corresponding surface treatment. In that sense, the recorded GIXRD patterns are representative of the crystalline phase composition and microstructural features for the near-surface region of these samples. The GIXRD patterns were acquired at the 33-BM-C beamline at the Advanced Photon Source facilities at ANL., using a double crystal monochromator with λ = 0.7749 Å with an incidence angle of 1°, with a step size of 0.001°. For that radiation energy and incidence angle, the estimated penetration depth in Nb is no deeper than 1 μm. The diffraction patterns were recorded by cooling from 300 to 30 K, at temperature intervals of 25 K, for every 10 min at each temperature, and then, the patterns were recorded again while the sample was warming up to 300 K. For GIXRD data processing, the background was removed first, and the qualitative phase analysis was carried out based on the ICDD and ICSD database, and an exhaustive patterns evaluation was performed in terms of their matching with the expected crystalline phases. Once the potential phases were identified, their cell and cell parameters were checked using DicVol and Le Bail programs available in the FullProf suite package [1].

RESULTS AND DISCUSSION

Tetrahedral and Octahedral Interstitial Sites in the Nb bcc Unit Cell

The Nb bcc unit cell has small available spaces with four and six Nb atoms as first neighbors, known as interstitial tetrahedral and octahedral sites, respectively (Fig. 1). The tetrahedral site has the smaller free volume related to a minor distance between neighboring Nb atoms. These sites are appropriate to accommodate small atoms, like hydrogen. The octahedral site has a relatively larger available volume for the absorption of bulky atoms, e. g. N, and O. The covalent radius of H, N, and O is 0.037, 0.077, and 0.066 nm, respectively. The distance between the centers of the neighboring tetrahedral and octahedral and tetrahedral sites is about ~0.019 and ~0.024 nm. This suggests that when the Nb metal has N or O as absorbed species, it could have a high ability to stabilize H atoms in the neighboring tetrahedral site, through a covalent interaction between them, N-H, or O-H. This occupying mechanism suggests

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that cavity performance can be improved with N or O doping to immobilize the absorbed hydrogen atom, limiting the H atom diffusion within the Nb matrix until reaching defect sites in the Nb network appropriate to the hydride precipitation.

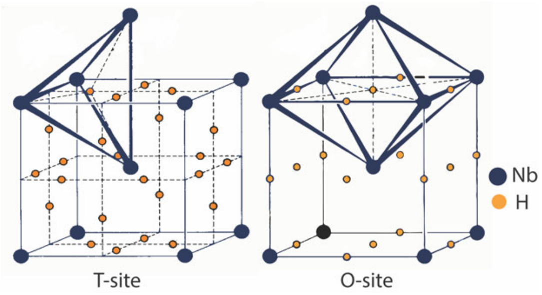

Figure 1: Interstitials tetrahedral (left) and octahedral (right) sites in the bcc Nb lattice.

EP+ 75/120 C Phase Composition

During the entire range of the cooling/warming cycle, the XRD pattern from the cutout EP+75/120C corresponds= to a single cubic phase, with a unit cell parameter **a** = 0.3315 nm. This is a typical value of metallic Nb. This Nb phase has a full width at half maximum (FWHM) of 0.31 °/2θ, about 2.5 times the one observed for the 800 + EP cutout, which is 0.12 °/2θ. Such a large FWHM is ascribed to the presence of lattice strain, probably related to the absorption of oxygen atoms in the octahedral interstitial sites. This will be congruent with the reported depth profile SIMS data for that sample [2], which that reveal a predominant presence of O atoms as absorbed species. Oxygen as a bulky atom, 0.066 nm, is enough to generate local strains in the Nb lattice. In the XRD pattern of this cutout appears a weak reflection with **d** = 0.2115 nm. This reflection could be assigned to the (111) plane of an fcc unit cell with a cell edge **a** = 0.3635 nm, which correspond to the values reported for α-Nb(OH_x) [3]. This assignment is in accordance with the presence of oxygen atoms in octahedral interstitial sites. The absorbed hydrogen atoms occupy the neighboring tetrahedral sites and remain trapped in the Nb network, with less feasibility to migrate to form hydrides upon the sample cooling. No precipitation of hydrides was observed in this cutout below 250 K. Below this temperature, in case of the hydrogen presence in Nb like 800C + EP cutout, the precipitation of hydrides was detected (see Fig. 4). Then, on the sample warming above that temperature, the hydrides were dissolved, and the hydrogens were re-absorbed into the Nb matrix, also this behavior was observed in the XRD pattern. When the cell edge was calculated from the recorded XRD pattern in the range of 30-300 K temperature, the sample cooling and warming, a regular cell contraction and expansion was observed (Figs. 2 and 3), respectively, without the presence of inflection that could reveal the occurrence of segregation or redissolution of secondary phases upon cooling. A peak broadening in XRD can also be related to a small crystallite size, below 100 nm. Such a possibility was discarded because a peak width of 0.15°/θ results in estimated crystallite size of 40 nm, using the Scherrer equation [1], well below to the reported from structural studies of SRF-grade Nb cutouts [4].

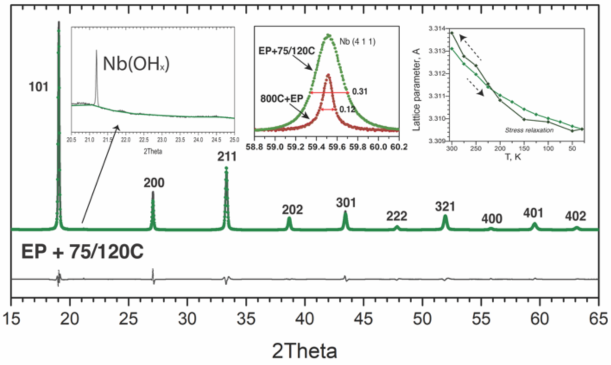

Figure 2: GIXRD pattern for the EP+75/120 ºC cutout recorded at 150 K. This pattern is composed of by reflections from Nb (bcc cubic phase) and of the second cubic phase (fcc) ascribed to the presence of α-Nb(OH) (Inset). The Nb phase shows a monotonous (regular) cell contraction and expansion during the cutout cooling and warming, respectively.

N-Doping (800C + 2/0 N) Phase Composition

The recorded GIXRD pattern for this cutout is composed by the presence of reflections to Nb (bcc unit cell) with **a** = 0.03317 nm and α-Nb(NH_x) and two minor phases, ascribed to NbN (hcp, **a** = 0.539 nm and **c**= 0.499 nm) and $NbNH_x$ (hcp, **a** = 0.3069 nm, **c** = 0.5091nm). This last phase appears reported for the Nb-N-H system [5]. The formation of this solid solution of Nb with N and H in interstitial positions is congruent with the relatively short distance between tetrahedral and octahedral sites, of about 0.020 nm, which makes possible a relatively strong covalent interaction between N and H atoms. This interaction could explain the advantage of N-doping for trapping H atoms. N atoms in the octahedral sites are energetically favorable to trap absorbed H atoms, so that no hydride precipitates can be form upon cryogenic cooling.

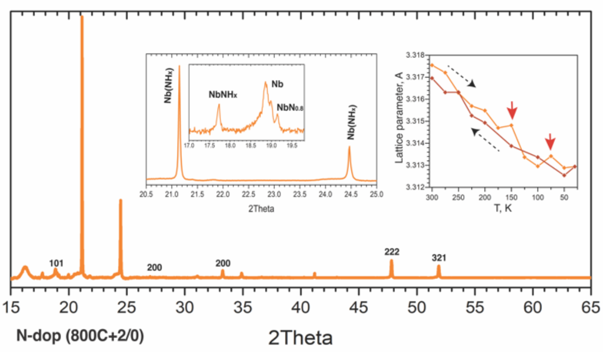

Figure 3: GIXRD patterns for the N-dop (800C+ 2/0) cutout recorded at 150 K. The main phases identified in this sample are Nb, and the solid solution α-Nb(NH_x), accompanied by two minor phases, $NbN_{0.84}$ and $NbNH_x$. Insets: (Right) Unit cell contraction and expansion during sample cooling and warming, respectively; (Left) reflections from α-Nb(NH_x) phase.

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800C + EP Phase Composition

Three minor phases were observed on this cutout; α-Nb(OH$_x$) same as the identified in the EP+75/120 ºC sample, plus two other phases that appear at low temperature, α-Nb(H) and β-NbH$_x$ (Fig. 4), with cubic (bcc) and orthorhombic unit cell, respectively.

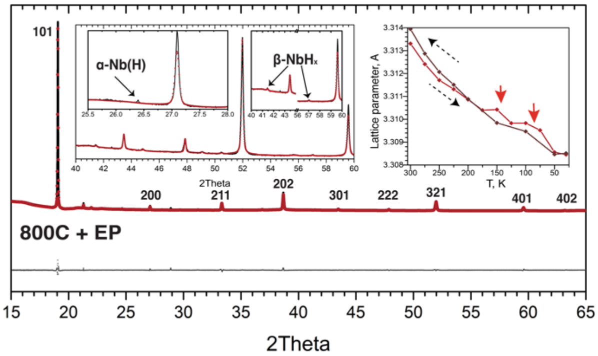

Figure 4: GIXRD pattern for the 800C + EP cutout recorded at 150 K. Two different secondary phases were identified, the α-Nb(H) solid solution with H atoms occupying the interstitial sites in the bcc unit cell of Nb, and the β-NbH$_x$ hydride, which appears as a segregated phase upon the sample cooling below 200 K (left inset). These hydride phases dissolved at 225 K while the sample warming. The right inset shows the unit cell contraction and expansion upon cooling and warming, respectively. The indicated inflections suggest that at these temperatures certain irreversible structural changes could be present.

The cell edge for that cubic phase is slightly larger (**a** = 0.3380 nm) than the one observed for the Nb matrix (**a** = 0.3315 nm). This solid solution remains stable below 150 K, which is not a typical of a hydride phase. Above that temperature, this weak reflection is probably found at the pattern background level. That reflection has been ascribed to such solid solution [6]. The cell parameters found for the β-NbH$_{0.89}$ phase (**a** = 0. 484 nm, **b**= 0.490 and **c** = 0.345 nm) are like the values reported for the corresponding file with ICSD collection code 150604. This hydride precipitates below 200 K on cooling and disappears at lower temperatures (< 150 K), dissolved to form other hydride modification (ε, δ, and λ), but with insufficient reflections another hydride phase has not been clearly identified. On the low angle region for the pattern of this cutout, the presence of NbF$_4$ was identified, indicating that during the EP treatment fluorine ions remain trapped in the Nb defects and finally appear as that phase. Fluorine forms soluble salts with Nb and from this fact it is used as a component in the EP process.

CONCLUSIONS

We have performed a crystalline structural study on cutouts from the cavities processed with state-of-the-art RF surface treatments by applying grazing incident synchrotron (GIXRD). The cutout coupons were directly extracted from N-dop, low-T (75/120 ºC) bake, and standard-T EP'ed cavities fabricated at FNAL. 1) For N-doping, Nb favorably forms Nb(NH$_x$) solid solution, where the N atoms occupy the interstitial octahedral sites of the Nb lattice and trap hydrogen atoms located in the tetrahedral sites. This interaction avoids the formation of Nb-hydride upon cooling. 2) A similar effect has been observed by the existence of oxygen in Nb interstitial sites from the low-T (75/120 ºC) baked cutout. 3) Only for the standard T-EP'ed sample, the Nb-hydride formation was observed, which is significantly related to the presence of hydrogen atoms in the Nb lattice forming an ordered solid solution with Nb, α-Nb(H).

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