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Successful Nitrogen Doping of 1.3 GHz Single Cell Superconducting Radio-Frequency Cavities *

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A high intrinsic quality factor (Q_0) of a superconducting radio-frequency cavity is beneficial to reducing the operation costs of superconducting accelerators. Nitrogen doping (N-doping) has been demonstrated as a useful way to improve Q_0 of the superconducting cavity in recent years. N-doping researches with 1.3 GHz single cell cavities are carried out at Peking University and the preliminary results are promising. Our recipe is slightly different from other laboratories. After 250 μm polishing, high pressure rinsing and 3 h high temperature annealing, the cavities are nitrogen doped at 2.7–4.0 Pa for 20 min and then followed by 15 μm electropolishing. Vertical test results show that Q_0 of a 1.3 GHz single cell cavity made of large grain niobium has increased to 4×10^{10} at 2.0 K and medium gradient.

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Intrinsic quality factor (Q_0) is one of the most important parameters of superconducting cavities. A high quality factor can reduce the operation costs of superconducting accelerators and the cost for the cryogenic system. Standard surface treatment methods are developed to improve the performance of superconducting cavities, including buffered chemical polishing (BCP), electropolishing (EP), high temperature treatment, low temperature baking, high pressure rinsing (HPR), etc. Operation with Q_0 over 1×10^{10} is realized with standard treatments for long macropulse x-ray free electron laser (XFEL).[1] However, for a continuous-wave superconducting radio-frequency (SRF) accelerator, higher Q_0 is needed to reduce the cryogenic cost. In recent years, a nitrogen doping (N-doping) recipe was discovered by the Fermi National Accelerator Laboratory (FNAL) and developed by FNAL, the Thomas Jefferson National Accelerator Facility (Jlab) and Cornell University to improve Q_0 of superconducting cavities.[2] The value of Q_0 has been improved to higher than 3×10^{10} for 1.3 GHz superconducting cavities and the N-doping recipe was adopted as the baseline cavity surface processing protocol for linac coherent light source Ⅱ (LCLS-Ⅱ) in 2014.[3] However, up to now, there has not been any report of successful N-doping from other laboratories except FNAL, JLab and Cornell University.

China will construct or propose for the SRF accelerator based large scientific facilities such as the hard XFEL facility and circular electron positron collider (CEPC). High Q_0 of superconducting cavities is required to reduce operation costs for this kind of large machine. As a part of pre-research, the N-doping recipe has been investigated at Peking University with 1.3 GHz single cell cavities and the significant improvement of Q_0 was observed.

One large grain single cell cavity and two fine grain single cell cavities (S4, S7) fabricated with Ningxia Orient Tantalum Industry Co., Ltd. (OTIC) niobium are used for N-doping researches. The average grain size is about 50 μm for fine grain niobium and more than several centimeters for large grain niobium. The procedure of N-doping is more or less the same as the recipe of Jlab: (1) Buffered chemical polishing (BCP) 250 μm (for large grain cavity and S4) or BCP 150 μm+electropolishing (EP) 100 μm (for S7) to remove surface damage layer; (2) high pressure rinsing (HPR) to clean the residual acid at the surface; (3) 3 h annealing at 800℃ for large grain cavity and 950℃ for fine grain cavities (S4, S7); (4) nitrogen doping process at 800℃ for 20 min and annealing for 30 min; (5) EP 15 μm to remove the bad superconducting niobium nitride phases; (6) ultrasonic degreasing and HPR to remove the residual acid at the surface; and (7) assembling and vertical test to obtain Q_0 versus E_{acc} (accelerating gradient) curves.

The main difference between our procedure and published recipes is in the first step. Considering that a thickness of 250 μm polishing can remove the surface damage layer efficaciously,[4] we carry out 250 μm BCP or 150 μm BCP+100 μm EP for comparison instead of less than 200 μm as other laboratories did. In addition, we adopt 950℃ to anneal the fine grain cavities rather than 800℃ in other laboratories' recipes, because recent researches[5] show that 900℃ and 950℃ annealing before N-doping is necessary to eliminate flux pinning sites of cavities made of Ningxia fine grain niobium.

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There are two kinds of doping recipes, which are 'light doping' and 'heavy doping'. With the light doping proposed by FNAL, the cavity is doped with nitrogen for 2 min and followed by 6 min annealing in a vacuum, then EP 5–7 μm;[6] while for the heavy doping proposed by Cornell University, the cavity is doped with nitrogen for 20 min and annealed in a vacuum for 30 min, followed by EP 10–20 μm.[7] Because the EP device for our N-doping researches at this moment is a simple one and the polished thickness is hard to be controlled accurately, we chose a heavy doping recipe to process the cavities. Figure 1 is the chamber of a high temperature furnace for single cell cavities annealing. The ultimate vacuum of the furnace is 1×10^{-5} Pa. The main N-doping processes are as follows: firstly, the temperature is raised to 800℃/950℃ at the speed of 4.4℃/min. Then the cavities are annealed at 800℃/950℃ for 3 h under the vacuum of 10^{-4} Pa. For fine grain cavities, the temperature is cooled down to 800℃. After annealing, the cavities are doped with nitrogen gas evaporated from a liquid nitrogen tank for 20 min at a nitrogen pressure of 2.7 to 4.0 Pa and then kept at 800℃ for 30 min under a vacuum of 10^{-4} Pa. When doping is finished, the cavities are cooled down to 55℃ in a vacuum.

Fig. 1. High temperature furnace for single cell cavities annealing.

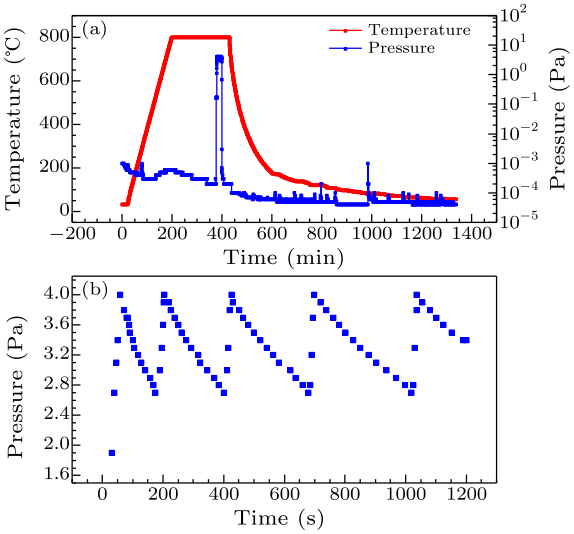

Fig. 2. (a) Variations of temperature and pressure during high temperature treatment. (b) Nitrogen pressure fluctuation during the N-doping process.

The variations of temperature and pressure during the processing are shown in Fig. 2(a). Figure 2(b) shows the nitrogen pressure fluctuation due to nitrogen absorption of the cavity during the 20 min N-doping process.

The final EP process was operated with the simple EP device. In this EP device, the acid was pumped into cavities through the cavity tube rather than a hollow aluminium bar (cathode), which is used in the standard EP device. Therefore, the flow rate of acid is hard to be controlled accurately. The voltage was set to 15 V in accordance to the optimum operation point in the current versus voltage curve plateau. Electrolyte temperature was controlled under 25℃. The rotation speed was about 1 rpm and the acid flow rate was about 3 l/min.

After N-doping treatment, the bad superconducting niobium nitride phases are formed near the surface of cavities and should be removed. Nitrogen concentration is mainly in the topmost 1 μm of the surface. A small amount of nitrogen is left deeper than 1 μm and serves as interstitial nitrogen in a niobium lattice,[2] which modifies the mean free path of a clean cavity surface. To analyze the concentration of nitrogen in N-doped niobium, we carried out time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements with some niobium samples, which are N-doped together with the cavities. The samples include one undoped sample, one N-doped sample without polishing and three N-doped samples electropolished with 7 μm, 15 μm and 25 μm, respectively. Figure 3 gives the results, showing that 15 μm EP is enough to remove the niobium nitride phase surface.

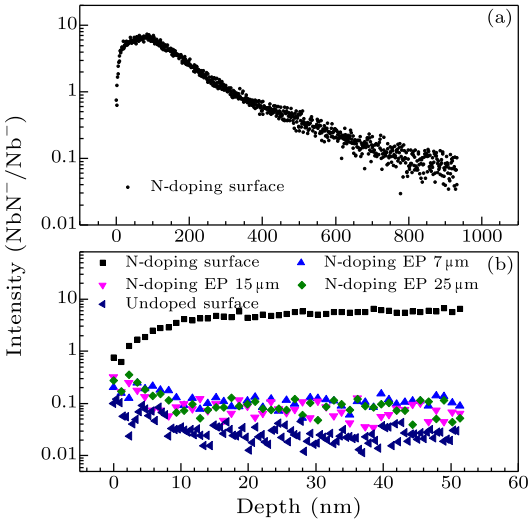

Fig. 3. (a) The relative concentration of nitrogen in the topmost 1 μm of N-doped niobium. (b) The relative concentration of nitrogen in an undoped niobium sample and N-doped niobium samples with different EP depths.

The N-doping cavities were tested with the vertical test system at Peking University. The cavities were cooled down as fast as possible to keep the high Q_0 since the N-doping cavities are sensitive to trapped magnetic flux.[8] The speed of cooling down through

transition temperature is about 18.3 mK/s. The test result for the large grain cavity is shown in Fig. 4. The value of Q_0 reaches 4×10^{10} at 2.0 K, 7×10^{10} at 1.8 K and 9×10^{10} at 1.6 K, when $E_{\rm acc}$ is around 12 MV/m. Those Q_0 values are obviously higher than Q_0 without N-doping. Anti-Q-slope, i.e., the increase of Q_0 with $E_{\rm acc}$ from the low field to medium field range, is also observed, which is the typical characteristic of N-doping cavities with the frequency of 1.3 GHz.[9]

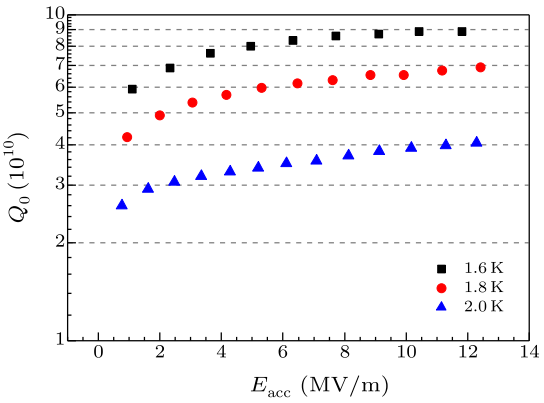

Fig. 4. The value of Q_0 versus $E_{\rm acc}$ at 1.6 K, 1.8 K and 2.0 K for the large grain cavity.

The value of Q_0 is inversely proportional to the surface resistance $R_{\rm s}$,

$$Q_0 = G/R_{\rm s}, \tag{1}$$

where $G = 270\,\Omega$ is the geometry factor of the cavity. The surface resistance $R_{\rm s}$ consists of two parts, temperature-dependent BCS resistance ($R_{\rm BCS}$) and material dependent residual resistance ($R_{\rm res}$),

$$R_{\rm s} = R_{\rm BCS} + R_{\rm res}, \tag{2}$$

$$R_{\rm BCS} = A\frac{\omega^2}{T}\exp\Big(-\frac{\Delta(0)}{kT_{\rm C}}\frac{T_{\rm C}}{T}\Big), \tag{3}$$

where T is the temperature, k is the Boltzmann constant, $T_{\rm C}$ is the critical temperature, ω is the frequency of cavity, $\Delta(0)$ is the energy gap at 0 K, A is the coefficient related to the London penetration depth λ, coherence length ξ_0 and mean free path l, and is influenced by the mean free path as follows:

$$A \propto \Big(1+\frac{\xi_0}{l}\Big)^{3/2}\frac{l}{\xi_0}. \tag{4}$$

If the mean free path is <10 nm (very dirty limit, 120℃ baking cavity) or >400 nm (very clean limit, EP/BCP cavity), BCS resistance is higher than that of the medium mean free path value.[2] N-doping treatment introduces a small amount of the nitrogen element into the niobium lattice. Interstitial nitrogen reduces the spacing between impurity scattering sites and brings the clean cavity surface to an intermediate mean free path range, which decreases the BCS resistance. In addition, interstitial nitrogen can prevent hydrogen from diffusing into niobium, thus decreases the rate of forming a weak superconducting niobium hydride phase, which degrades the Q_0 of superconducting cavities during the cooling down.

Figure 5 gives the measured Q_0 versus T curve of the large grain cavity. Parameters of the large grain cavity are obtained by fitting the curve with Eqs. (1)–(3) and calculating with the SRIMP code.[10] The energy gap $\Delta(0)$ is $1.83kT_{\rm C}$. The mean free path is 66 nm, which is in the intermediate range, $R_{\rm res}$ is 3.4 nΩ, and $R_{\rm BCS}$ is 3.3–5.9 nΩ at 2 K.

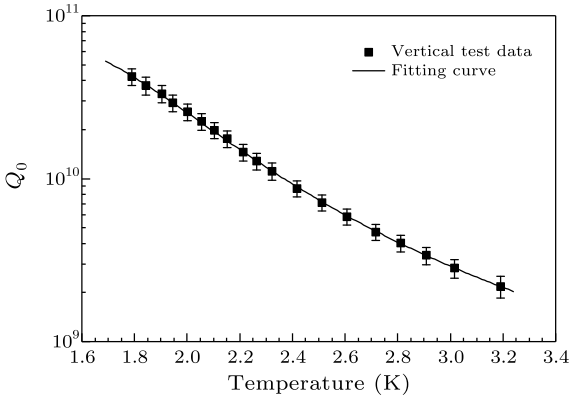

Fig. 5. The value of Q_0 versus T of the large grain cavity.

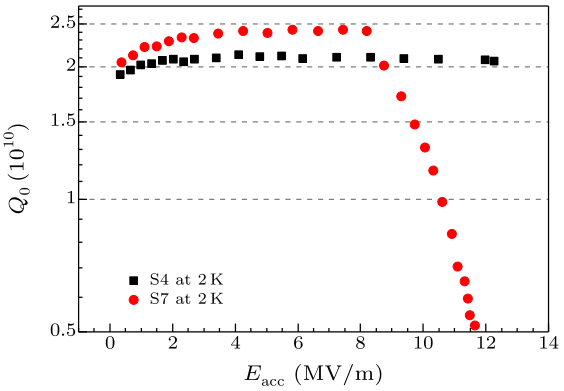

Fig. 6. The value of Q_0 versus $E_{\rm acc}$ at 2.0 K for the fine grain cavities S4, S7.

The results of N-doping for two fine grain cavities S4 and S7 (see Fig. 6) are not as good as the large grain cavity. However, the higher Q_0 and anti-Q-slope are also observed. The different performances between large grain cavity and fine grain cavities are probably caused by the density of pinning sites in OTIC niobium material. There are more grain boundaries, dislocations and impurities in smaller grain size niobium material, which serve as pinning sites to trap magnetic flux. The trapped magnetic flux increases the residual resistance.[11] For fine grain cavities, Q_0 of S4 is lower than S7. The difference between the surface treatment of these two cavities is the first step of the recipe. It seems that 100 μm EP before nitrogen doping is helpful to increase Q_0.

In summary, nitrogen doping has been successfully

realized at Peking University and the preliminary results show a prospective effect for improving the intrinsic quality factor of superconducting cavities. The improvement of Q_0 and anti-Q-slope are obvious especially for the large grain cavity. However, the maximum $E_{\rm acc}$ is lower than 13 MV/m and the main reason may be that the surface of the cavities was contaminated during the EP process with our current simple EP device. More experiments with the improved EP system will be carried out, and the high Q_0 at higher $E_{\rm acc}$ is expected.

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