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FLUX PINNING STUDY OF OTIC NIOBIUM MATERIAL*

Shu Chen, Jiankui Hao#, Shengwen Quan, Lin Lin, Kexin Liu
State Key Laboratory of Nuclear Physics and Technology & Institute of Heavy Ion Physics, Peking University, Beijing 100871, China

Abstract

The performance of superconducting cavities is influenced by the trapped flux during the cooling down through critical temperature, especially for nitrogen doped cavities which are more sensitive to flux trapping. We have investigated the flux trapping of OTIC niobium samples with different grain size. Samples were prepared and heat treated at 800 °C and 900 °C, followed with different surface removal by BCP. A series of measurements, including MPMS, TOF-SIMS, were carried out on the niobium samples. The results and analysis will be presented.

INTRODUCTION

Intrinsic quality factor Q_0 is one of the most important parameters of superconducting cavities. High quality factor can reduce the cryogenic load of superconducting cavity and reduce the considerable costs for the cryogenics. In 2012, FNAL colleagues discovered very high Q values on single cell cavities treated with nitrogen in high temperature furnace, which is called N-doping recipe [1] and discovered that "light doping" improves quench field while maintaining the benefit of high Q. Cornell colleagues found that "heavy doping", which needs longer nitrogen atmosphere and more EP removal, is effective to improve the performance of superconducting cavities. In 2014-2015, N-doping recipe was adopted as the baseline cavity surface processing protocol for LCLS-II [2].

It was reported that some superconducting cavities treated with 800 °C nitrogen doping recipe did not meet the spec of LCLS-II(2.7×10^{10} in 5mG field) [3]. To solve this problem, 900°C modified recipe was tried on material. Some material (ASTM<7.0) changed better, and met the high quality factor requirement. But some material (ASTM>7.0) did not change as much. After treated at 950°C and 970 °C, the material eventually can be used [3]. The difference in performance with different materials is caused by trapping magnetic flux. Flux expulsion behavior of cavities seems to be a great deal in different materials, even in batches from a single vendor. To investigate the problem, flux pinning study on OTIC niobium samples of different grain size and other vendor's niobium samples were carried out at Peking University.

Q_0 degradation by trapped flux can be considered as a three-step process [5]: 1.the cavity is cooled in external environment magnetic field B_{ext}. 2.some of the B_{ext} is trapped in cavity surface, called B_{trap}. 3.the B_{trap} introduces the residual resistance R_{res}, and increases the surface resistance R_s. So the quality factor of cavity is reduced. We focus on the second step, how much B_{ext} is trapped in the material. Some researches [3, 4] show that different niobium material has different flux expulsion behavior, and the flux expulsion behavior changes a lot after different temperature heat treatment. B_{trap} is the key factor to superconducting cavities whether N-doping works or not. We used the MPMS (Magnetic Property Measurement System) to measure the flux trapping in different samples, which can be helpful to understand the variability between the different materials and different treatments.

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#E-mail: jkhao@pku.edu.cn

PREPARATION AND TREATMENTS OF NIOBIUM SAMPLES

Preparation of Different Kind of Niobium Samples

Two fine grain niobium strips from different vendors were used for the investigation. One niobium strip has grain size ASTM 4.5-5.0 and hardness HV49.8. Another niobium strip has the same grain size ASTM 4.5-5.0. And a large grain niobium strip was taken into account. All samples are listed in Table 1. Small samples were cut out from these niobium strips by wire electric discharge machining. Then they were etched by BCP (1:1:2) with the depth of about 250μm, to remove the mechanical damage layer. We use pure water to rinse the samples and clean the surface sufficiently in case of remaining acid from BCP process. After pure water (ρ>2MΩ-cm) rinsing, the samples were moved to clean room, rinsed by ultrapure water (ρ>18MΩ-cm) again, followed by drying and annealing at 800° C for 3 hours. The vacuum of the furnace is 10^{-4} Pa. The samples were put on niobium sheets that had been BCP treated to prevent pollution, see Figure 1. The whole heating process was divided into 7 stages as follow.

- The pressure in the furnace was pumped to 1.2×10^{-4}Pa
- Heating from room temperature to 500 °C in 30 minutes.
- Maintaining at 500 °C for 60 min
- Heating from 500 °C to 800°C in 30 minutes.
- Maintaining at 800 °C for 180 min
- Cooling down in vacuum.
- When temperature down to 60 °C, open the furnace.

The maintaining at 500 °C and 800 °C helps to degas the impurity in the niobium material. At the end, all samples were etched 40 μm by BCP and rinsed by ultrapure water. After all the above steps were accomplished, grain size of FG1 samples decrease to ASTM 3.5-4.5. And grain size of FG2 samples decrease to ASTM 3.0-3.5. By annealing at

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800 °C for 3 hours, the grain size of FG1 samples became larger than that of FG2 samples, although they had the same grain size as received. The two samples were analysed by MPMS and TOF-SIMS, which will be explained in detail later.

Table 1: Preparation of Different Kind of Samples

Material	Grain size ASTM	BCP before annealing	Annealing	Grain size after annealing
FG 1	4.5-5.0	250 µm	800 °C/3h	3.5-4.5
FG 2	4.5-5.0	250 µm	800 °C/3h	3.0-3.5
LG	LG	250 µm	800 °C/3h	--

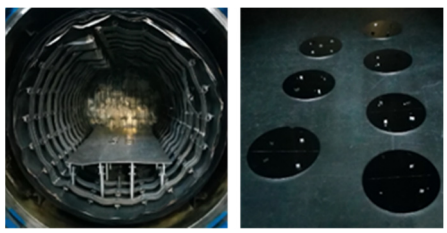

Figure 1: Samples were put on niobium sheets that had been BCP treated, and put in furnace.

Preparation of Niobium Samples with Different Grain Size

To investigate flux trapping property between samples with different grain size, we take samples from some batches of OTIC niobium material, as listed in Table 2. We also prepared large grain niobium samples named as F0, F1 and F3, which stand for large grain samples with no grain boundary, with only one grain boundary and with three grain boundaries, respectively. All the samples (A B C D F0 F1 F3) were handled as following steps: cutting out from niobium strips by wire electric discharge machining, BCP 250µm, ultrapure water rinsing, annealing at 800°C or 900°C for 3 hours, final BCP 40µm. We anneal the samples in a new furnace with Rhodes pump and cryogenic pump to avoid contamination. The samples with different grain size and heat treatment are listed in Table 2.

Preparation of Nitrogen Doping Niobium Samples

The flux expulsion is nearly the same for cavities with similar bulk history regardless of surface conditions [5]. Whether the samples are N-doping or not, they should have the same magnetic flux expulsion property. But there is no direct evidence that the same magnetic flux is trapped. We prepared nitrogen doping niobium samples with different grain size to analyze their trapped flux by MPMS. Three OTIC samples with different grain size were prepared, see Table 2. All samples above were handled as following steps: cutting out from niobium strips, BCP 250 µm, ultrapure water rinsing, annealing in 800 °C for 3 hours, injecting nitrogen for 20 minutes, 800 °C annealing in vacuum for 30 minutes, cooling down in vacuum. Figure 2a shows the temperature and pressure during the nitrogen doping treatment. After annealing at 800 °C for 3 hours, nitrogen was injected to the furnace for 5 times. The nitrogen pressure was controlled between 2.7 Pa (20 mTorr) and 4.0 Pa (30 mTorr) during 20 minutes. The detail about nitrogen injection is shown in Figure 2b. The nitrogen doping niobium samples are list in Table3.

Table 2: Preparation and Treatment of Samples with Different Grain Size

Material	Grain size ASTM	BCP before annealing	Annealing	BCP after annealing	Number
NX FG	4.5-5.0	10/150/200/250 µm 250 µm	None 800 °C/3h	None 40 µm	A
NX FG	5.0	250 µm	800 °C/3h 900 °C/3h	40 µm	D
NX FG	6.0	250 µm	800 °C/3h 900 °C/3h	40 µm	B
NX FG	6.5-7.5	250 µm	800 °C/3h 900°C/3h	40 µm	C

Table 3: Preparation of Nitrogen Doping Niobium Samples

Material	Grain size ASTM	BCP before annealing	Annealing	Number
NX FG	4.5-5.0	250 µm	800°C/3h+N20min+A30min	A-N20
NX FG	6.0	250 µm	800°C/3h+N20min+A30min	B-N20
NX FG	6.5-7.5	250 µm	800°C/3h+N20min+A30min	C-N20

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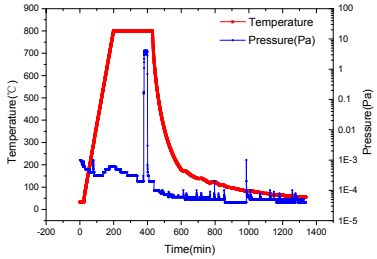

Figure 2a: Temperature and pressure during the nitrogen doping treatment.

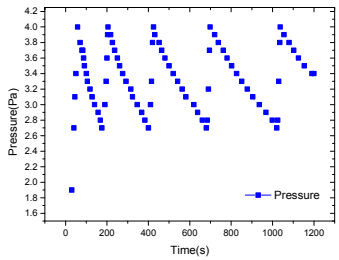

Figure 2b: The detail about nitrogen injection.

RESULTS AND DISCUSSIONS

MPMS Analysis

The trapped flux of niobium samples was measured using Quantum Design Magnetic Property Measurement System. The MPMS uses superconducting Quantum Interference Device (SQUID) to measure DC magnetization. The system was demagnetized from 30000O_e and cooled down in zero field to 2K. The external magnetic field was ramped up above H_{c2} about 4500Oe and ramped down to zero. The hysteresis (irreversible magnetization) in magnetization curve is caused by vortex pinning in bulk niobium [6]. In detail, the hysteresis curves indicate the magnetization behavior of samples in superconducting state. The irreversibility in magnetization is consistent with the vortex pinning of the type-II superconductors, smaller pinning sites density leads to smaller area of the hysteresis loop [7]. Pinning sites could be voids, impurities, dislocations, grain boundaries, inclusion, etc [8]. So the area of the hysteresis loop reflects the density of the pinning sites.

Figure 3a shows the flux trapping is influenced by surface damage layer. Niobium samples of OTIC were cut from the same fine grain niobium strip whose grain size is ASTM 4.5-5.0. These samples were etched by BCP with different depths, 10 μm, 150 μm, 200 μm, 250 μm. With no annealing, the samples were measured by MPMS to get their hysteresis loop. The sample with 10μm BCP trapped more flux than others because of surface damage layer. Several flux jumps were observed in the magnetization data of this sample. And its H_{ffp} (which is H_{c1} for reversible curve) and area of hysteresis loop is larger than others. When the samples were BCP 150 μm, the flux jumps disappeared, and hysteresis loop became more smooth and smaller. The deeper the samples were etched, the less pinning sites the samples would leave. The sample with BCP 250μm had the smallest hysteresis loop, and was considered to remove all of surface damage layer.

Variety of different kinds of niobium samples is showed in Figure 3b. FG1 samples, LG samples and FG2 samples were treated in the same steps, BCP 250μm followed by annealing at 800 °C for 3 hours. LG material had the smallest hysteresis loop because of its less grain boundaries and defects. FG1 material has more pinning sites than FG2 material, which can be seen from their different hysteresis loop. When turned into superconducting state, FG1 material will trap more flux and degrade the superconducting property. The varieties of pinning sites density may be caused by different amount impurities from vary materials. The impurities study of them was carried out by TOF-SIMS, and will be discussed in the next part.

Figure 3c shows that flux trapping is influenced by grain size. Different grain size niobium samples, D (ASTM 5.0), B (ASTM 6.0), C (ASTM 6.5-7.5) were BCP 250μm and annealed at 800°C for 3 hours. For sample C, grain size is smaller, and there are more grain boundaries in the same volume. The hysteresis loop of sample C is larger than D and B. Grain boundaries acting as pinning sites in bulk niobium trap more flux. That is why superconducting cavities made from small grain size (ASTM>7) material expel flux more difficult. After 900 °C heat treatment, small grain size material recovers its flux expulsion behavior and reduces the pinning sites. In Figure 3d, small grain size sample C has nearly the same hysteresis loop with sample D and B after 900 °C annealing. So, for small grain size material to nitrogen doping, 900 °C high temperature annealing may be helpful to expel more flux. Some strange phenomenon are discovered. 900 °C high temperature annealing may increase the pinning sites in larger grain size material (ASTM<5.5). In Figure 3e, the hysteresis loop of sample D (ASTM 5.0) after 900 °C annealing becomes larger than that after 800°C annealing. In extreme situation, large grain niobium material appears the same rules. The large grain samples after annealing appear larger hysteresis loop than that after 800°C annealing, which is shown in Figure 3f. 900 °C high temperature heat treatment increases the pinning sites and help to trap more flux in larger grain size material(ASTM<5.5) and large grain material. The reason is not clear at the moment and the study is under way.

Figure 3g,h,i indicate that flux trapping is influenced by nitrogen doping treatment. We found that hysteresis loop of nitrogen doped samples are larger than that of undoped samples. The value of H_{ffp} and H_{c2} of different grain size samples would be larger for nitrogen doped samples. The nitrogen doping treatment increases the pinning sites in the material and traps more flux. It is caused by nitride on sample surface, because the samples were not electropolished after nitrogen doping. The samples with EP are being prepared and the properties will be measured in the next step.

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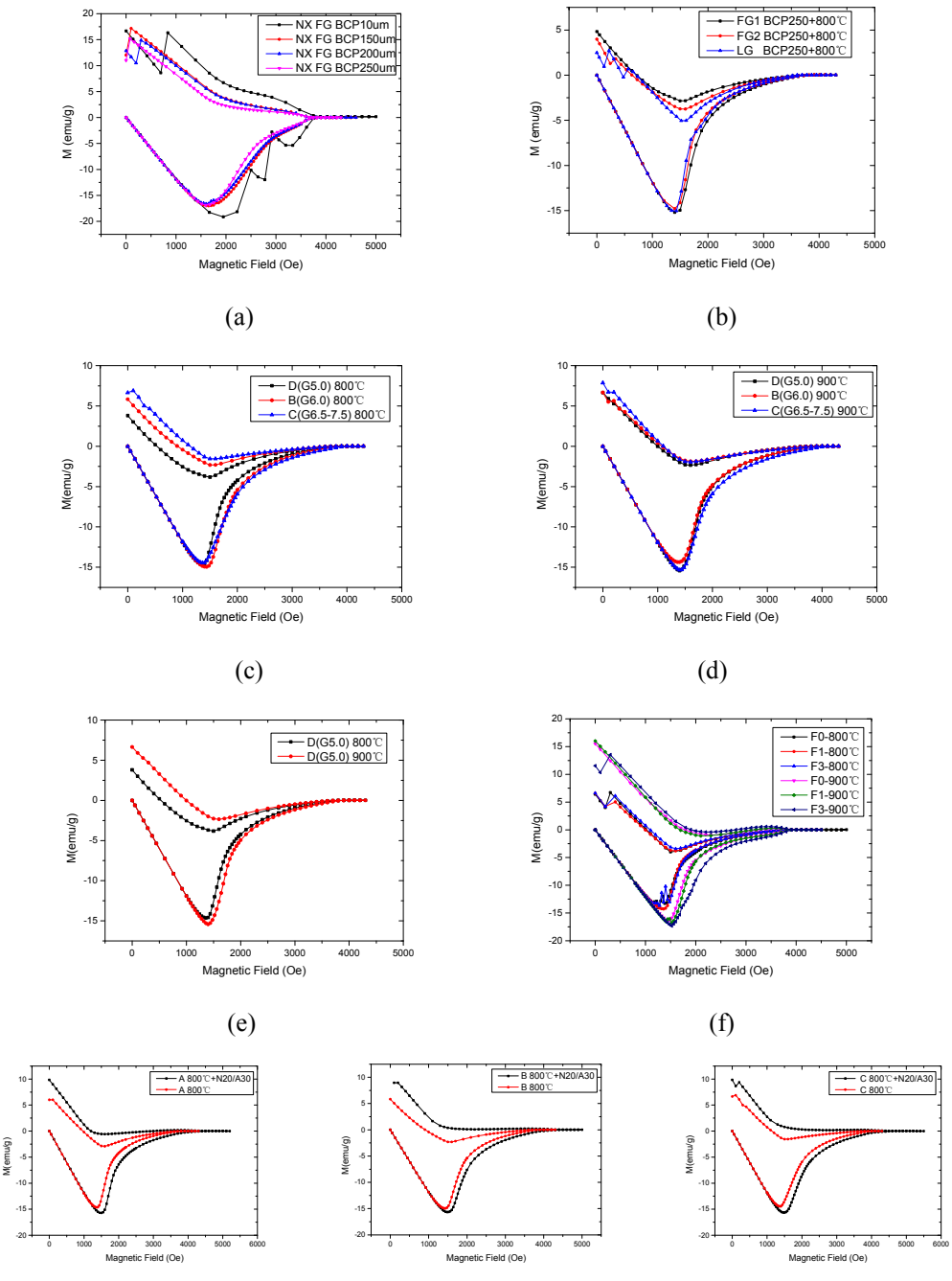

Figure 3: MPMS measurement result of all samples.

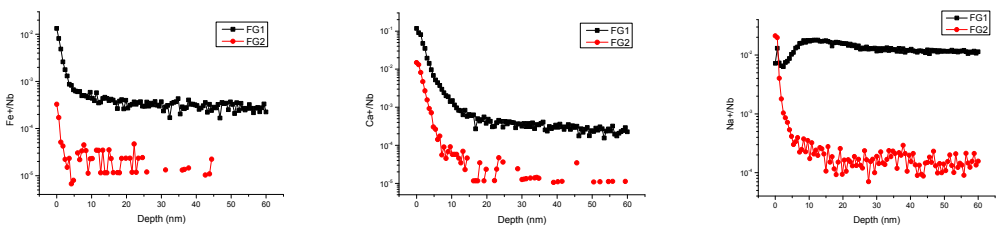

Figure 4: TOF-SIMS measurement result of different material.

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TOF-SIMS Analysis

TOF-SIMS was used to measure the various impurity content of FG1 and FG2. O sputtering ion beam was used to sputter the material layer by layer with 0.6 nm/s. Bi primary ion beam was used to detect elements such as Fe, Ca, Na, Ta, Mo and Nb since O negative ion enhances the positive ion yields. The raster area was 300μm×300μm with the detected area of 100μm×100μm. The depth was about 60nm with respect to SiO_2 substrate. The detected elements between different samples may have tiny difference. So the measured value of each impurity element was normalized with niobium.

From the measured results, Ca, Fe in FG1 material are 20 times higher than that of FG2 material (Figure 4ab). Na in FG1 material is 100 times higher than that of FG2 material (Figure 4c). And other metallic element, such as Ta, Mo, Ti in FG1 material are also higher than that of FG2 material (which are not listed in Figure). The metallic element may be pinning sites in material to trap flux and make the difference. The metallic element impurity content plays an important role in material flux expulsion behavior.

CONCLUSION

Flux pinning study on OTIC niobium material was carried out at Peking University. To find out the factors that influence material pinning sites density and flux trapping property, different kinds of niobium samples with different treatments were measured by MPMS and TOF-SIMS. We found that the flux pinning in material is influenced by following factors: 1.damage layer on material surface. Samples with deeper etched by BCP would leave less pinning sites. 250 μm BCP is considered to remove the surface damage layer efficaciously. 2.impurity content in material. FG1 have more pinning sites than that of FG2 material. TOF-SIMS measurement shows that there is more metallic element content in FG1 material. These metallic impurities may act as pinning sites to trap flux. 3.grain size and grain boundary. After 800 °C annealing, the pinning sites in larger grain size material are less than that in small grain size material. And small grain size material is more difficult to expel the flux. 4.high temperature heat treatment. For smaller grain size material, 900 °C high temperature annealing may reduce the pinning sites, and can compare with the larger grain size material in flux expulsion behavior. But for larger grain size (ASTM<5.5) fine grain material and large grain material, 900 °C high temperature annealing may increase the pinning sites, and trap more flux in material. 5.nitrogen doping treatment. The material with nitrogen doping traps more flux than undoped material, regardless of grain size. The study on flux pinning may help us to understand the mechanism of cavity flux expulsion behavior and optimize the nitrogen doping program.

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