MODIFICATIONS OF SUPERCONDUCTING PROPERTIES OF NIOBIUM CAUSED BY NITROGEN DOPING OF ULTRA-HIGH QUALITY FACTOR CAVITIES*

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Abstract

A study is presented on the superconducting properties of niobium used for the fabrication of the SRF cavities after treating by recently discovered nitrogen doping methods [12]. Cylindrical niobium samples have been subjected to the standard surface treatments applied to the cavities (electro-polishing, low temperature bake-out) and compared with samples treated by additional nitrogen doping recipes routinely used to reach ultra-high quality factor values (over $3{\cdot}10^{10}$ at 2 K, 16 MV/m). The DC magnetization curves and the complex magnetic AC susceptibility have been measured. Crosscheck resistivity measurements of the critical surface magnetic field (B_{c3}) are also presented.

Evidence for the lowered field of first flux penetration after nitrogen doping is found confirming the correlation with the lowered quench fields. Superconducting critical temperatures T_c = 9.25 K are found to be in agreement with previous measurements. Wider transition gap for nitrogen treated samples is observed. No strong effect on the critical surface field from nitrogen doping is found. The results of B_{c3} measurements via AC susceptibility are confirmed by resistivity measurements.

In addition, the results of low energy muon spin rotation (LE-μSR) spectroscopy measurements of magnetic field penetration into superconducting niobium are presented. A strong correlation between London penetration depth behavior and niobium treatment is demonstrated. Such behavior is in agreement with anti-Q-slope effect measured previously.

INTRODUCTION

Superconducting radio frequency (SRF) cavities are the key technology for future particle accelerators for high-energy physics, nuclear physics, light sources, and accelerator-driven subcritical reactors. Several decades of SRF research and development at laboratories and universities worldwide have led to the successful realization of niobium cavities that reliably achieve very high gradients and quality factors.

Recent breakthrough discovery at Fermilab demonstrated positive impact on cavity's quality factor from the doping of certain amount of nitrogen into niobium cavity walls. However, this treatment reduces somewhat the maximum gradient achievable in the cavity, i.e. reduction of quench field takes place. It was demonstrated that SRF cavities, which surfaces prepared with electrolytic polishing (EP) method and low temperature (120ºC) bake-out for 48 hours, can have quench fields over 40 MV/m, while cavities which undergone nitrogen doping are limited by a quench field of 25-30 MV/m. [1, 12]

Magnetic measurements on niobium samples are a useful tool to investigate the effect of nitrogen doping on niobium critical fields. The experimental studies on the magnetization and susceptibility of niobium samples presented in the paper have been carried out with the aim to gain an understanding of superconducting properties change by nitrogen doping.

MAGNETOMETER EXPERIMENTAL PROCEDURE

The samples for the magnetization and susceptibility measurements are cylinders with diameter of 2.85 mm and a height of 7.0 mm, which are cut from RRR~300 fine grain niobium sheets used for SRF cavity production. Bulk EP of about 120 µm removal was done on all samples. After that, one of the samples was baked for 48 hours at 120ºC in the vacuum. Such surface preparation in SRF cavities typically leads to maximum accelerating fields of 40 MV/m and above. Two other samples are prepared using different nitrogen doping recipes, which found to deliver SRF cavities with optimal quality factor (over $2.7{\cdot}10^{10}$ and above at 2 K, 16 MV/m). The procedure of surface treatment (after initial bulk EP) is the following:

- high temperature bake at 800ºC for 3 hours in vacuum;
- bake at 800ºC for time t_1 with nitrogen gas in the chamber (diffusion of nitrogen into niobium happens);
- after diffusion bake at 800ºC for time t_2 in vacuum (diffused nitrogen redistributes inside the niobium walls to produce desired nitrogen concentration profile);
- 5 µm surface layer removal by EP (nitrides formed at the surface removed, desired surface concentration of nitrogen is achieved).

Time parameters t_1 and t_2 are subject to optimization. Optimal in terms of quality factor recipes have the following parameters: t_1 = 2 min, t_2 = 6 min and t_1 = 20 min, t_2 = 30 min. Cavities prepared with the first recipe have quench fields of up to about 30 MV/m. Cavities prepared with the second recipe have quench fields of up

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to about 25 MV/m. One more presented sample had no extra treatment after bulk EP.

Sample DC magnetization is measured with a commercial magnetometer (Quantum Design PPMS) at 2 K in external DC magnetic field between zero and 1 T. The same system is also used for AC susceptibility measurements. A frequency of 10 Hz and AC field amplitude of 0.2 mT allow good noise suppression and an acceptable measurement time. In all measurements external magnetic fields are aligned parallel to the symmetry axis of the cylindrical samples.

The demagnetization factor was calculated according to the theoretical expression [2]

$$N_Z = 1 - \frac{1}{1 + \frac{d}{h}\left(\frac{4}{3\pi} + \frac{2}{3\pi}\tanh\left(1.27\frac{h}{d}\ln\left(1+\frac{d}{h}\right)\right)\right)},$$

where d is a diameter of the sample and h is its height. For the given samples $N_Z = 0.195$. The magnetization and susceptibility data presented below have been corrected using this demagnetization factor.

CRITICAL TEMPERATURE

The superconducting transition temperature T_c is determined from the onset of the screening component χ' of the complex AC susceptibility $\chi = \chi' - i\chi''$ measured at zero DC field as a function on temperature (Fig. 1). Critical temperature of all measured samples is about 9.25 K.

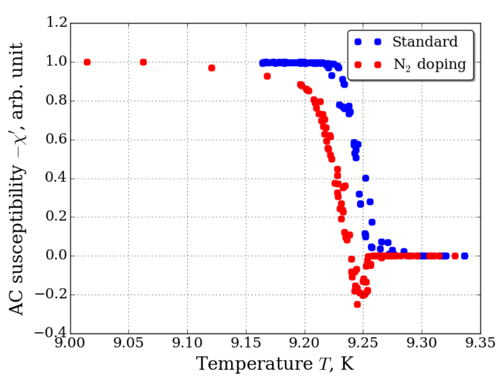

Figure 1: Real part of the linear AC susceptibility measured near zero-field transition temperature of the niobium samples. All considered samples have critical temperature about 9.25 K. The width of transition region depends on existence of normal conducting fractions at the surface of the superconductor.

Figure 1 shows screening component of the AC susceptibility as a function of temperature for baked sample and the sample treated with nitrogen before final EP. Transition zone for the latter sample is wider than for the baked sample. This is explained by existence of normal conducting nitrides at the surface of the nitrogen treated sample.

Imaginary part of AC susceptibility χ'' in normal conducting state determined during this measurement. Its value used to determine critical surface field during the AC susceptibility measurements at 2 K.

MAGNETIZATION MEASUREMENTS

DC magnetization measurements result of the first three samples described in Section "Experimental procedure" is shown in Fig. 2. Magnetization and external magnetic field corrected using demagnetization factor such that in Meissner state their sum is equal to zero. This fact represents magnetic field expulsion from the superconductor.

Penetration of magnetic field into the superconductor leads to the deviation of magnetization curve from a straight line. The deviation is greater when more magnetic flux penetrates the superconductor. Magnetization is equal to zero when external magnetic field is higher than upper critical field B_{c2}.

Figure 2 demonstrates that magnetic flux starts entering the superconductor at lower fields for nitrogen doped samples as compared to the low temperature baked one. Moreover, magnetic flux enters at lower fields for the sample exposed to nitrogen for 20 minutes as compared to the one exposed to nitrogen for 2 minutes only.

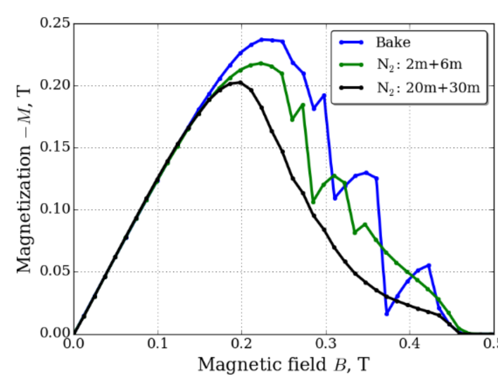

Figure 2: DC Magnetization of niobium samples as a function of external magnetic field at 2 K.

SRF cavities performance prepared according to these three recipes is presented in [1]. Low temperature baked cavities can reach quench fields of 35 MV/m and above. Cavities exposed to nitrogen for 2 minutes are found to have maximum quench fields of about 30 MV/m. Cavities prepared by the recipe assuming nitrogen exposure for 20 minutes can reach quench fields of 25 MV/m. Due to the cavity configuration, these values transform to 170 mT, 130 mT and 107 mT penetration magnetic field (i.e. external magnetic field when magnetic flux enters niobium), correspondingly. Further investigation is required to determine the exact relation between quench and amount of magnetic flux penetrated, but obtained results allow ordering the samples by quench field based on magnetization curves.

There is no clear effect of nitrogen doping on the upper critical field, but it is found that nitrogen doping reduces the field of first flux penetration, likely a cause of the decrease of the quench field in nitrogen-doped SRF cavities.

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SURFACE SUPERCONDUCTIVITY

Saint-James and de Gennes [3] discovered the nucleation of superconducting regions in a thin surface sheath at magnetic fields higher than the upper critical magnetic field. Surface superconductivity can be observed in the field range from upper critical field B_{c2} to critical surface field B_{c3}. Such behavior is observed in all considered samples. The value of critical surface field can be determined from the measurement of complex AC susceptibility as a function of external magnetic field.

Such measurement was done for all four samples described in Section "Magnetometer experimental procedure": low temperature baked sample, two nitrogen doped samples and the electro-polished one. Imaginary and real parts of susceptibility measurements are shown in Fig. 3 and 4 respectively. When external magnetic field reaches the critical value B_{c3}, imaginary part of susceptibility becomes equal to its value in normal conducting state (measured in Section "Critical temperature") and absolute value of real part of susceptibility abruptly drops down to zero.

Both real and imaginary parts are shown in arbitrary units, but they have different normalization. Imaginary part is divided by its value in normal conducting state, such that at external magnetic field higher than B_{c3} normalized value is one. Real part of susceptibility is normalized such that its maximum absolute value is one.

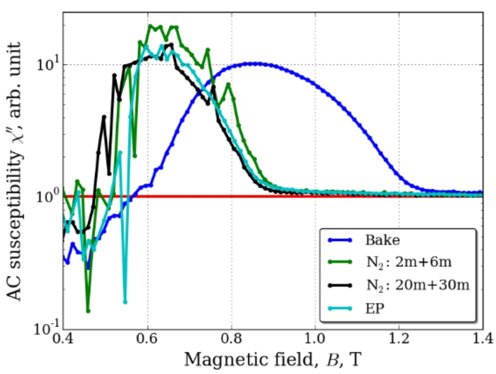

Figure 3: Field dependence of the imaginary part of AC susceptibility of niobium samples with different surface treatments. The data has been taken at 2 K, frequency is 10 Hz, AC field amplitude is 0.2 mT.

One can see that electro-polished and nitrogen doped samples demonstrate similar behavior, while low temperature baked sample behaves differently. Critical surface field for the sample undergone low temperature bake is significantly higher than for the other samples. It means that unlike low temperature bake, nitrogen doping does not significantly change microscopic parameters of the superconductor surface, such as an electron mean free path.

As shown in [4] the ratio r_{32} between surface critical field and upper critical field depends on the surface preparation but not on the temperature. From presented measurements for low temperature baked sample r_{32} = 2.6, which is in agreement with the results presented in [4]. The ratio for other samples r_{32} = 2.0 is also in a good agreement with measurements of [4] for electro-polished samples.

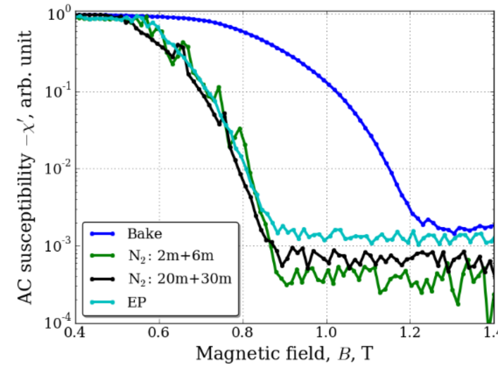

Figure 4: Field dependence of the real part of AC susceptibility of niobium samples with different surface treatments. The data has been taken at 2 K, frequency is 10 Hz, AC field amplitude is 0.2 mT.

Another way of measuring the critical surface field is direct resistivity measurements in external magnetic field (Fig. 5). Varying the external magnetic field from zero to 3.0 T, a jump in resistance around 1.3 T was observed. A decay in real part of AC susceptibility was observed at the same value of external magnetic field, which confirms the results of B_{c3} measurements.

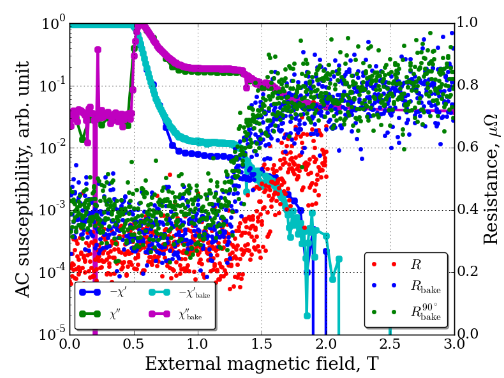

Figure 5: Real part of AC susceptibility and resistance of niobium samples with different surface treatments as a function of external magnetic field. Susceptibility data has been taken at 2 K, frequency is 10 Hz, AC field amplitude is 0.2 mT. The results of resistance measurements are in agreement with the susceptibility measurements results.

LOW ENERGY MUON SPIN ROTATION

Low energy muon spin rotation (LE-μSR) is a unique technique to perform precise microscopic measurements of the magnetic field profile inside superconductor. It recently has become available at the μE4 beam line at PSI. LE-μSR unmatched sensitivity was demonstrated on thick niobium films in the clean limit. This technique is an ideal probe to address the problem of understanding the difference in microscopic superconducting properties of niobium affected by different treatments.

The Meissner–Ochsenfeld effect [5], stating that at low frequencies and magnitudes of external magnetic field a superconductor expels or excludes any magnetic flux from its core, is a fundamental property of a superconductor. However, the magnetic field penetrates at the surface of the superconductor. The magnetic penetration depth is a typical length scale on which the field penetrates. A good approximation of the magnetic field dependence on depth for a large scale of superconductors is exponential one. It is derived for a semi-infinite superconductor in the London limit [6]. The approximation does not always hold for impurity doped type I superconductor. It was demonstrated by Pippard on a set of microwave experiments in [7].

In analogy with the anomalous skin effect Pippard introduced the concept of nonlocal response of the superconductor, i. e., the screening current trying to expel the magnetic field must be averaged over some spatial region of the order of ξ called the coherence length. The physical interpretation of ξ is, that it is the length over which the superconducting wave function can be considered as rigid, i. e., roughly speaking the size of a Cooper pair. The nonlocal electrodynamic response leads to various modifications of the London theory, one being that the magnetic penetration profile $B(z)$ is no longer exponential and even changes its sign beneath the surface of the superconductor. All these findings were confirmed by the microscopic BCS theory [8]. Although these theoretical predictions have been known for half a century, only very recently has a "direct" measurement of the functional dependence of $B(z)$ been demonstrated using LE-μSR. For example, the results providing a direct and quantifiable measure of nonlocal effects in investigated materials and allowing the extraction of physical parameters such as the magnetic field penetration depth and the coherence length ξ are published in [9] and [10].

For SRF technology purpose the superconducting properties within 130 nm from the surface can be directly revealed with LE-μSR. This is achieved by measuring the magnetic field inside the superconductor as a function of depth.

Theoretical background is described in details in [11]. The parameter which is discussed in the paper is London penetration depth in Pippard model. It is directly proportional to the London penetration depth parameter used in assumption of exponential magnetic field penetration inside superconductor.

The LE-μSR technique uses beams of 100% spin-polarized positive muons (μ^+), which serve as sensitive local magnetic probes when implanted inside a sample. At the μE4 beam line at PSI, a high intensity surface muon beam with an energy of about 4 MeV is moderated to ultra-low epithermal energies (about 15 eV) in a cryogenically condensed solid argon film deposited on a 10 K–cold argon foil. These epithermal muons are subsequently accelerated by electrostatic fields to energies up to 30 keV, corresponding to implantation depths of up to about 140 nm in niobium.

Upon implantation, the muon precesses in the local magnetic field at its stopping site. The precession frequency is proportional to the magnetic field and is measured by detecting the anisotropic muon decay (lifetime 2.2 μs): the decay positrons are preferentially emitted in the direction of the μ^+ spin, which allows to monitor the time evolution of the muon spin by registering the positrons in detectors surrounding the sample. Analyzing the data collected from multiple muons, it is possible to extract the magnetic field penetration profile inside the superconductor along with intrinsic characteristics of the superconducting material [11].

Initially unexpected behavior of London penetration depth as a function of local magnetic field was noted in [11]. In the given paper, the detailed analysis of LE-μSR data is presented. In addition, a comparison of nitrogen-doped samples with baked ones is presented (Fig. 6).

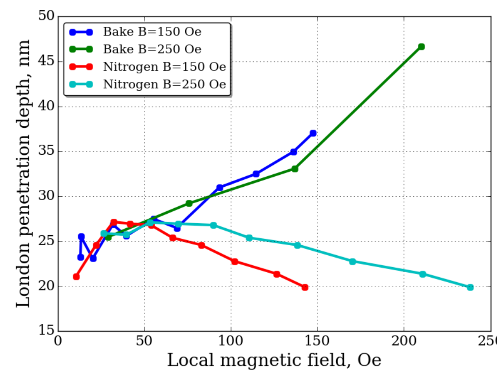

Figure 6: London penetration depth as a function of local magnetic field measured with LE-μSR for niobium samples – cut-outs from actual SRF cavities treated by low temperature bake-out and nitrogen doping. External magnetic field of 150 Oe and 250 Oe was applied to each sample.

Figure 6 demonstrates the effect of nitrogen doping on London penetration depth behaviour with local magnetic field. For the niobium samples without nitrogen penetration depth increases with increase of local magnetic field. For the samples treated with nitrogen doping, the London penetration depth decreases with local magnetic field starting from about 50 Oe.

Further detailed quantitative analysis is required to relate directly the London penetration depth and quality factor of the cavity, but given result qualitatively is in agreement with previously published measurements of quality factor of baked and nitrogen doped SRF cavities (Fig. 7). Figure 6 displays that penetration of magnetic field decreases with increase of external magnetic field. Increase of external magnetic field is the same as increase of accelerating field. Decrease of magnetic field penetration leads to lower power losses in the surface of superconductor, which means higher values of the quality

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factor. As a result, there is an anti-Q-slope of the excitation curve.

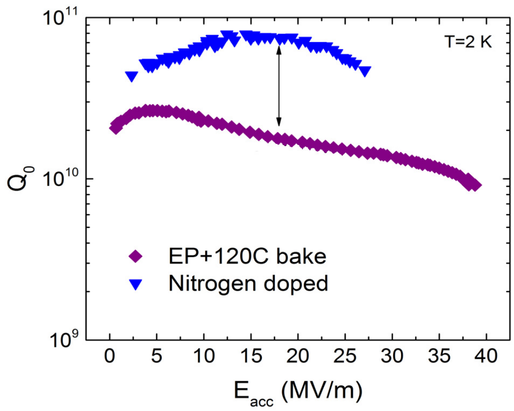

Figure 7: Excitation curves (quality factor as a function of accelerating field) for SRF cavities undergone low temperature bake-out and nitrogen doping surface treatments. Along with other effects of nitrogen doping medium field anti-Q-slope is observed (in the range of accelerating field from 5 to 15 MV/m).

CONCLUSION

Measurements of magnetization curves and complex AC susceptibility for the niobium samples with different surface treatments including nitrogen doping are presented.

Significant effect of nitrogen doping on the field of first flux penetration into the superconductor is observed. The decreased values of this field are likely the cause of the decreased quench field of SRF cavities produced according to the investigated recipes.

There is no significant effect of nitrogen doping on the surface critical field B_{c3} observed, which suggests that microscopic parameters such as the mean free path at the surface are not as strongly affected as in the case of low temperature bake. This results are confirmed with both AC susceptibility and resistivity measurements.

The results of LE-μSR measurements of magnetic field penetration inside superconducting niobium are presented. There is significant difference in the behavior of London penetration depth as a function of local magnetic field for low temperature baked and nitrogen doped cavities is observed. This difference is in qualitative agreement with previously published results of the quality factor measurements. Nitrogen effect on London penetration depth parameter might be a clue in explanation the anti-Q-slope of the excitation curve, but further detailed investigation is necessary.

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