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NIOBIUM SAMPLE ANALYSIS FOR NITROGEN INFUSION AND DOPING

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Abstract

KEK has been investigating the better conditions of the heat treatment in nitrogen, which are called as nitrogen doping and nitrogen infusion. We have tried to understand the high gradient performance of the cavity from the analyses of samples which were prepared in the same conditions for the cavity. The main tools are D-SIMS for the depth profile of the elemental concentration, XPS for composition analysis and SQUID magnetometry for the critical DC magnetic field measurement. The difference in the depth profiles of the nitrogen, car-bon and oxygen between the heat treatment conditions, containing the degree of vacuum and furnace temperature of nitrogen injection, was observed by GD-OES, D-SIMS and XPS. Such a difference correlates with the vortex penetration field measured by SQUID. In particular, that of the nitrogen doping sample was greatly degraded, while that of the nitrogen infusion sample was slightly improved. The tendency is consistent with the RF high gradient test results.

NITROGEN TREATMENT AT KEK

The nitrogen heat treatment can improve the performance of superconducting RF (SRF) cavities. There are two ways for nitrogen treatment. One is the nitrogen doping (N-dope), in which the sample is doped with nitrogen heavily during annealing the cavity at a high temperature in the vacuum furnace and then the heavy doped layer is removed by the electropolishing (EP) [1]. The other way is the nitrogen infusion (N-infusion), in which nitrogen is infused into the sample at a low temperature after annealing the cavity without expose the cavity to the air [2]. In both methods, the oxidized surface layer is removed by high temperature annealing before nitrogen treatment. KEK also succeeded in N-dope and N-infusion using the J-PARC furnace which is equipped with oil free pumps [3, 4]. However, N-infusion decreased the Q value in some cases. In order to investi-gate the cause for the decrease in Q, we installed the niobium reference samples to the furnace together with the cavies and analysed them. First, the samples were cut out of the fine grain niobium sheet produced by the Tokoyo Denkai Co Ltd, which is followed by the EP or chemical polishing (CP) process to remove the surface layer by about 100 µm. Then, the samples were subjected to almost the same heat treatment as the cavity.

DEPTH PROFILE OF N-DOPE

The depth profile of the N-dope sample was measured by the GD-OES (HORIBA, Ltd GD-Profiler 2). The discharge gas was argon. The measured area was 4 mmΦ in the sample with a size of 50×50×3 mm^3. Figure 1 shows the depth profiles of the N-doped and the annealed samples for reference. As shown in Fig. 2 for the temperature and vacuum trend, the N-dope sample was first annealed at 800 °C in a vacuum of 1×10^{-4} Pa for 3 hours and then was doped in 3 Pa nitrogen for 20 minutes, which is followed by the diffusion process of nitrogen to the inner in a vacuum for 30 minutes. No additional EP was applied after heat treatment in both samples. From the data in Fig. 1, it is obvious that the nitrogen doping occurs at least up to 30 µm in depth for the N-dope sample. However, the carbon doping also seems to occur in both samples. We suspected the nitrogen purity in the furnace was poor because a small portable pump was used instead of the main pumps, which were off during nitrogen injection in order to avoid the failure of main pumps. The reached pressure of the small portable pump was 1×10^{-3} Pa. The surface distribution of the carbon can be also seen using the SEM (Hitachi High-Tech Corp., SU6600) in which EDS sensor can be insert from the horizontal axis to the sample surface with the large capture solid angle. Figure 3 shows the reference SEM and EDS image of another N-dope sample prepared in the KEK small furnace which is equipped with an oil diffusion pump. In this case, the carbon distribution is more clearly observed. The carbon seems to be absorbed to the grain boundary. However, the Q-value of the N-doped cavity using J-PARC furnace was improved after EP by several µm. We think that the effect of N-infusion is more sensitive to carbon pollution because the heat treatment affects the final surface.

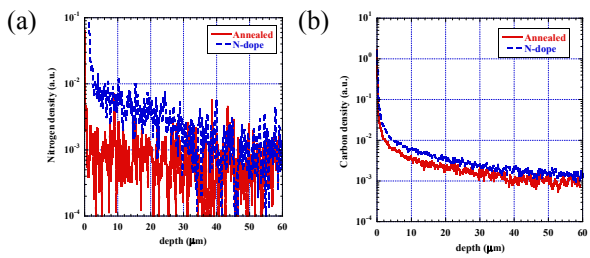

Figure 1: Depth profile of N-dope and annealed samples. (a) nitrogen, (b)carbon.

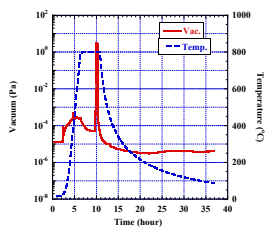

Figure 2: Heat treatment trend of the N-Dope.

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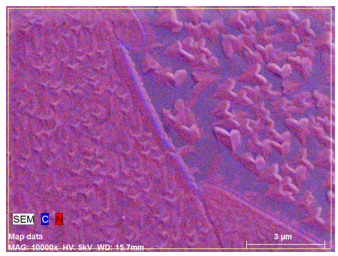

Figure 3: SEM/EDS image of the N-dope sample treated at KEK small furnace using oil diffusion pump. Blue and red show the carbon and nitrogen distribution respectively.

N-INFUSION

The first N-infusion using the J-PARC furnace degraded the *Q* value and gradient. This is due the slow pumping speed during nitrogen injection, resulting in the rather high base pressure of 1×10^{-3} Pa. Hence, the pumping speed was improved for the second N-infusion with a low base pressure of 1×10^{-5} Pa. Figure 4 shows the temperature and vacuum trend of the second N-infusion. In this process, the nitrogen was infused at 120 ºC with the pressure of 3 Pa for 48 hours after the sample was annealed at 800 ºC for 3 hours and cooled down. The difference between the first and second processes of the N-infusion is only the base pressure during nitrogen injection.

The depth profiles of the N-infusion and the annealed samples for reference were measured by dynamic SIMS (ULVAC Phi, Inc.) and XPS (ULVAC Phi, Inc. Versa Probe). The sample size is $7\times7\times3$ mm^3 both for SIMS and XPS. In the SIMS measurements, we used the primary ion beam of Cs^+ with the accelerating voltage of 500 V causing a sputtering rate of 0.015 nm/s. In the XPS measurement, the Al Kα X-ray source with the spot size of 200 μmΦ and the power of 45 W was irradiated with sputtering to take the depth profiles. The sputtering speed was 2.3 nm/min, which was calibrated by using SiO_2 standard sample. Figure 5 shows the comparison of the depth profiles measured by the SIMS for the annealed, first N-infusion and second N-infusion samples, respectively. The nitrogen is obviously infused for the N-infusion samples. The nitrogen infused depth of the first N-infusion is deeper than that of the second N-infusion. The carbon density at 15 nm depth of the first N-infusion sample is higher than other two samples. The oxygen profiles are also much different among three samples. The depth profiles measured by XPS also show the same tendency (Fig. 6). We suspect the large infused depth of oxygen or carbon as the cause of the *Q* degradation in the first N-infusion sample. It is necessary to perform the same measurements using the number of samples with various condition to identify the cause.

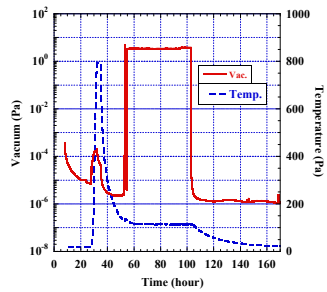

Figure 4: Heat treatment trend of the N-infusion.

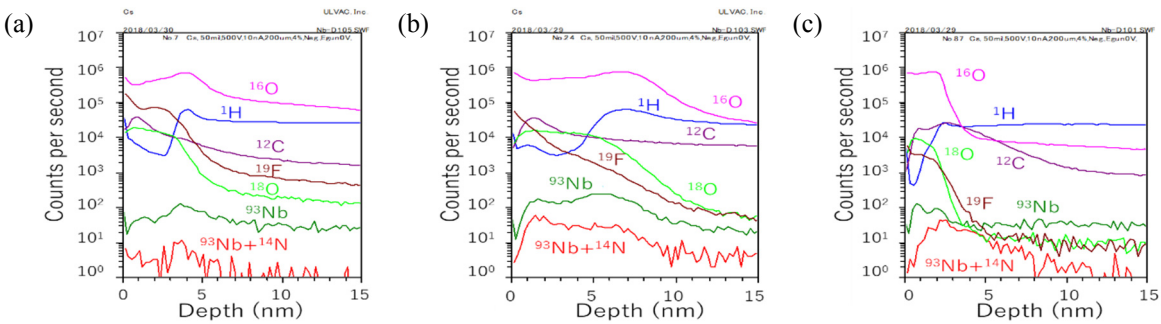

Figure 5: Dynamic SIMS measurement (a)annealed, (b)1st N-infusion, (c) 2nd N-infusion.

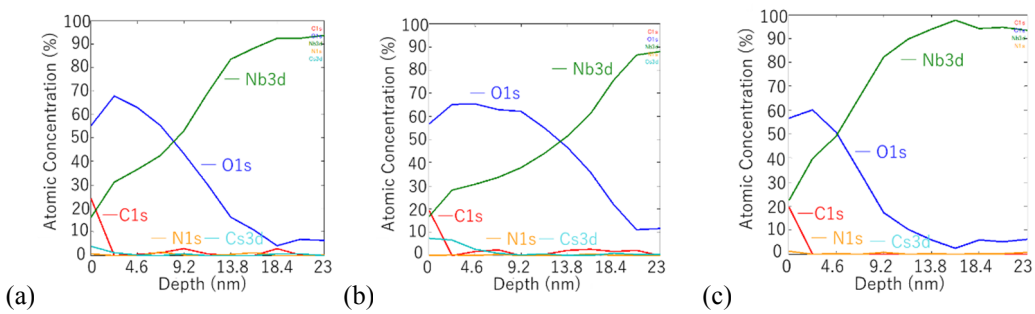

Figure 6: XPS measurements (a) annealed, (b)1st N-infusion, (c) 2nd N-infusion.

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DC CRITICAL FIELD MEASUREMENT

The maximum gradient of the cavity is closely related to the vortex penetration field (H_{vp}), which can be measured under a static magnetic field [5]. We compared the H_{vp} values for the annealed (800 °C × 3 hours in vacuum), N-dope and N-infusion samples using the SQUID magnetometer (see Fig. 7) (Quantum Design Inc. MPMS). For the correct comparison, the samples were shaped into a 2 mmΦ sphere. In this case, the demagnetization coefficient of 1/3, leading to the diamagnetic enhanced factor of 150 %. Fabrication error of the sample is 5 μm and the maximum ratio of the vertical and horizontal diameter is 1.005. The enhanced factor is estimated using CST studio (Fig. 8). The error of the enhanced factor is 0.3 %. This value corresponds to 3.6 Oe against the measured H_{vp} of ~1200 Oe, which is small enough as mentioned later. All the samples were polished by 100 μm in terms of CP and heat treated. In addition, the additional 20 μm and 10 μm CP were applied to the annealed and N-dope samples, respectively.

Figure 9 shows the magnetization vs. field (M-H) curves for all the samples measured at 2 K. The measurement range of the magnetic long moment was fixed, because the measurement values became discontinuous at range switching. Therefore, error is large at low field.

In order to distinguish the H_{vp}, $(2M/3\text{-}H))/H$ was calculated from the fact that the demagnetizing magnetization $2M/3$ by the Meissner effect is equal to the external field. Figure 10 shows the $(2M/3\text{-}H)/H$ curves. Edges of H_{vp} are clear in the annealed and N-infusion samples, while H_{vp} of the N-infusion sample is a little higher. On the other hand, it is clearly observed that the vortices penetrate slowly into the N-dope sample, resulting in the difference in H_{vp} of ~200 Oe between the N-infusion and the N-dope samples. The results indicate that the surface barrier of the N-infusion sample is higher than the annealed sample and that of the N-dope one is much lower, which is in the similar tendency to the RF high gradient test results.

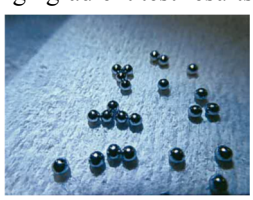

Figure 7: Niobium samples for SQUID.

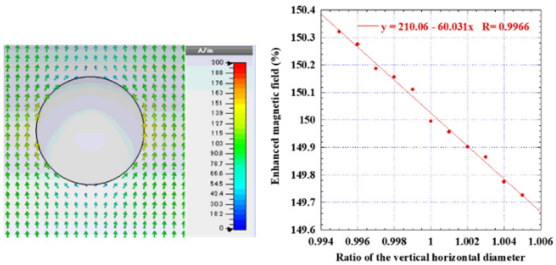

Figure 8: CST simulation of the enhanced factor.

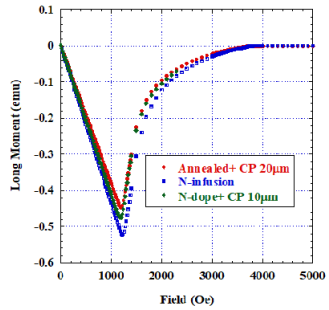

Figure 9: M-H curves of the samples.

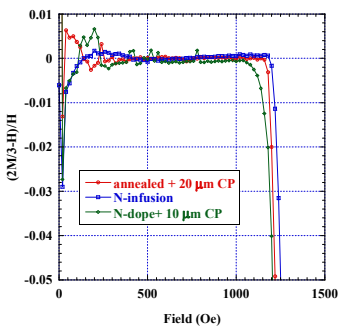

Figure 10: $(M\text{-}H)/H$ curves.

SUMMARY

KEK has been investigating the better nitrogen treatment conditions. N-infusion degraded the Q-value in some case at KEK. We suspect that the oxygen infused depth or the carbon density is the cause in the examinations by SEM/EDS, SIMS and XPS analysis. In addition, the difference of the H_{vp} value between the N-dope and N-infusion samples derived by the SQUID measurements is consistent with the vertical test results.

ACKNOWLEDGEMENTS

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