DEVELOPMENT OF HYDROGEN-FREE EP
AND HYDROGEN ABSORPTION PHENOMENA*

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Abstract

Annealing has been applied to eliminate absorbed hydrogen for the superconducting niobium cavities. Absorbed hydrogen causes performance degradation of cavities. For a large-scale production, time-consuming annealing process costs a lot. We have searched for a hydrogen absorption mechanism and finally innovated hydrogen-free electropolishing (EP).

We found the reason for hydrogen absorption: hydrogen is picked up from the polishing liquid (water) during Centrifugal Barrel Polishing. We have innovated the hydrogen-free CBP by exchanging water for a liquid containing no hydrogen component. In addition, we made clear that niobium picks up hydrogen from EP acid very easily through damaged niobium surface and the stationary chemical oxidation process can prevent the hydrogen absorption in such a case. We thus invented the hydrogen-free EP by adding a little amount of nitric acid into the EP acid as the oxidizer. Using the combination of the hydrogen-free CBP and the hydrogen-free EP, we have finally developed an annealing free process. We have demonstrated high gradient of 30MV/m can be attained by this method on an L-band single-cell niobium cavity. This method can bring a big cost saving in large-scale production like TESLA.

INTRODUCTION

Mechanical grinding is a powerful method to remove surface defects from superconducting niobium cavities. We developed a simple and fast mechanical grinding method: CBP (Centrifugal Barrel Polishing) [1], as the pre-treatment for EP. Continuous horizontal EP process, which is present KEK standard process, was developed during R&D period for TRISTAN [2]. Electropolished surface is smoother than that by chemical polishing (CP). Today, the superiority of EP over CP on the performance of niobium cavities has been widely recognised [3].

Since the TRISTAN project, we have been applying the combination of mechanical grinding and EP, where annealing process was inevitable to eliminate hydrogen Q-disease. This annealing is time-consuming and pushes the preparation cost high. For a large-scale production like TESLA, if possible it should be eliminated for cost-reduction. We studied hydrogen Q-disease. Using a new 1300MHz (L-band) niobium single-cell cavity with RRR (Residual Resistivity Ratio) = 200, we checked whether

the hydrogen Q-disease would occur with the TRISTAN EP method if annealing process was omitted. The hydrogen problem was not observed on the cavity after removing approximately 200μm from the surface. Outgassing sample test also detected no hydrogen after removing 150μm [4]. We confirmed that the continuously applied electric potential during EP is effective to prevent hydrogen absorption.

We applied the combination of CBP and EP to another L-band niobium cavities. This resulted in a heavy hydrogen Q–disease. As no hydrogen problem was found with the continuous EP, it must have been caused by the CBP. We applied the CBP on niobium test samples and observed hydrogen having been absorbed. This evidence pushed us to further studies on hydrogen absorption mechanism. Finally we understood the source of the hydrogen is the water used in the CBP and established the hydrogen-free CBP replacing the water by a hydrogen-free polishing liquid, FC-77.

We applied the combination of this hydrogen-free CBP and the continuous EP. This however resulted in heavy hydrogen Q-disease. The hydrogen must have been absorbed through surface defects caused by the CBP. We also confirmed that hydrogen Q-disease did not occur with a combination of the hydrogen-free CBP and CP. The CP acid contains nitric acid acting as oxidizer. While EP acid contains no such oxidizing chemicals. This suggests that the oxidation could prevent the hydrogen absorption. In the EP, oxidization occurs only when electric voltage is applied. In the current EP process in KEK, prior to applying the heavy EP, we remove surface contamination due to the CBP by light EP (so called the pre-EP) and dump the EP acid. Since we close the EP acid in the cavity during the pre-EP,
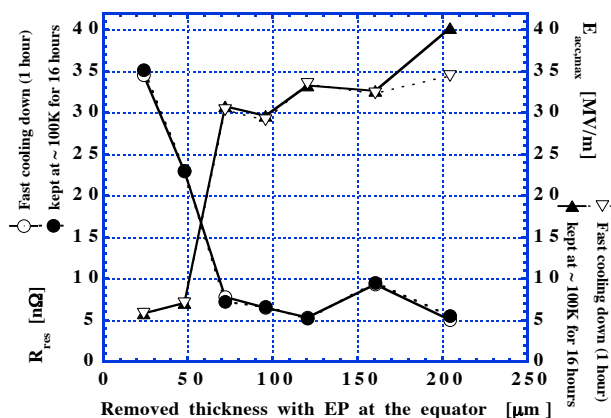

Figure 1: No Hydrogen Q-disease with massive 200μm material removal with EP.

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the acid temperature often goes up to 37°C. There is a time when the damaged surface is exposed to the EP acid with no oxidation process, so that hydrogen absorption would be promoted by such a high temperature acid. We applied the pre-EP using a new EP acid dropping a bit of nitric acid in order to have the continuous oxidization process, then made the main EP using the conventional EP acid. As the result, we could successfully prevent the hydrogen absorption and achieved the high accelerating gradient of 30MV/m with an L-band single-cell cavity.

EXPERIMENTS

Evaluation method of Hydrogen Q-disease

The degree of hydrogen Q-disease is dependent on the amount of absorbed hydrogen in the niobium material and the time the cavity is exposed at the dangerous temperature region, around 100K [5, 6]. Hydrogen Q-disease appears as the degradation of Q_0 value, corresponding to an increased surface resistance. We define our evaluation procedure on the degree of hydrogen Q-disease as following:

1) at first, we cool down the cavity by the fast cool down in an hour from 300K to 4.2K, then we measure the temperature dependence of the surface resistance and take Q_0–Eacc excitation cure at 1.5K as the reference performance,
2) then the cavity is warmed up to 100K and exposed the temperature for 16 hours,
3) after this, the cavity is cooled down again to 4.2K by the fast cool down and the second set of measurements are repeated.

Measurement of hydrogen in a niobium sample

Hydrogen concentration in niobium test samples is measured by hydrogen gas chromatography, melting the niobium. Data analysis was done with LECO Co. Model RH-404. The measurement procedure is shown in Figure 2. In this method, the information is the amount of hydrogen in whole the bulk: the average value over whole the bulk. We made thin samples of 1.0mm thick in order to enhance sensitivity for the hydrogen trapped on surface.

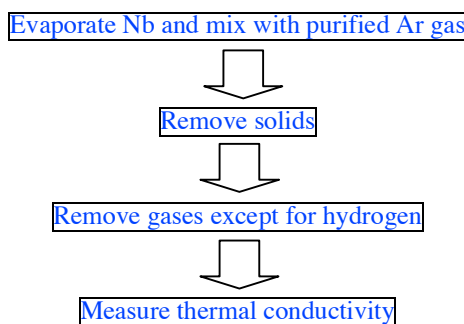For the sample preparations, we well degassed

Evaporate Nb and mix with purified Ar gas

Remove solids

Remove gases except for hydrogen

Measure thermal conductivity

Figure 2: Measurement of amount of hydrogen in a niobium sample

hydrogen from the material by annealing (at 750°C for 3 hours at a base pressure of 1x10^{-6} torr) before the subsequent experiments. We thus kept the initial hydrogen concentration in the samples less than 1ppm. Appling the CBP to samples, we made ultrasonic rinsing after that to remove the abrasives, which might include hydrogen. Successively the CBP we treated the samples by various methods. We kept the samples in nitrogen gas atmosphere until the hydrogen analysis. The accuracy of the measurement is 1 to 2 ppm. We observed a good agreement between the degree of hydrogen Q-disease of the cavity and hydrogen concentration of test samples by the same treatment [4].

RESULTS AND DISCUSSION

Hydrogen absorption during the CBP

As mentioned above all samples and cavities were annealed before the measurement to remove ambiguity in measuring the amount of absorbed hydrogen. A cavity was treated by the combination of 30μm CBP (GCT media 2150g, water 850cc with detergent, 160rpm, 4hours) and 50μm EP. The result showed a heavy hydrogen Q-disease as seen in Figure 3. From this result and the previous test results in Figure 1, the CBP must have induced hydrogen absorption. We put niobium samples (2.5mm x 1.0mm x 147mm, RRR = 200) in a niobium cavity during the CBP process. We measured hydrogen concentration in the samples. It was 78ppm. We thus confirmed serious hydrogen absorption by the CBP.
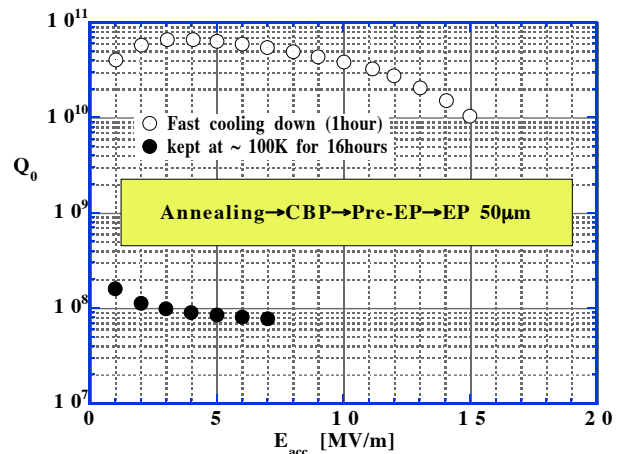
Figure 3: Heavy hydrogen Q-disease did occur in combination of CBP and EP

To understand this hydrogen absorption mechanism, we studied the effect of water used for the CBP. The result is shown in Table 1. In the case of water without detergent, the hydrogen concentration was 79ppm and no difference from our standard CBP case i.e. the mixture of water and detergent. The detergent thus has no effect on the hydrogen absorption. In the case of absence of water, i.e. media only, hydrogen concentration was reduced remarkably and was 11ppm. This concludes that the absorbed hydrogen came from the water used in the CBP.

Table 1: Absorbed hydrogen during 4hrs of various CBP

Liquid used in CBP	Hydrogen concentration in the test sample	Removed thickness from the cavity wal	Comments
Water and detergent	78.0 ± 2.9ppm	30μm	Standard composition
Water	79.1 ± 5.0ppm	29μm	No detergent
No liquid	10.9 ± 0.8ppm	~0μm	Solid media only
Propanol	49.4 ± 2.2ppm	31μm	No water
FC-77 (C_8F_{18} , C_8F_{16}O)	4.6 ± 0.8 ppm	20μm	No hydrogen
10% hydrogen peroxide	28.4 ± 1.4ppm	24μm	Oxidation effect

(Measurement of hydrogen concentration was repeated ten times over each sample)

The above evidence suggests that the damaged niobium surface during the CBP picks up hydrogen from water. If this assumption is correct, the amount of absorbed hydrogen will depend on the hydrogen bonding energy of various liquids used. We compared water with propanol which has a different bonding energy for hydrogen. Though the amount of absorbed hydrogen was reduced when the propanol was used, still a lot of hydrogen (60% of the water case) was detected. The best way is to use a hydrogen-free liquid. Fortunately we can commercially obtain such a liquid e.g. FC-77 (mixture of C_8F_{18} and C_8F_{16}O, a product of the 3M Co.). With the FC-77, hydrogen concentration was reduced dramatically and was 5ppm. Thus we innovated a hydrogen free CBP using the hydrogen-free liquid.

Combination of hydrogen-free CBP and EP

We expected the combination of the hydrogen-free CBP and EP would solve the hydrogen problem. We applied this combination on an L-band cavity. The actual procedure consists of the following: 1) after the hydrogen-free CBP, the cavity was rinsed with FC-77, 2) pre-EP was applied to remove only a couple of micron from the surface. If making the main EP successively the CBP, the EP acid is contaminated by the abrasives in the CBP. Therefore we applied a light EP without circulating the acid and dumped the contaminated acid. 3) The following main EP removed 50μm thickness with the acid circulating.
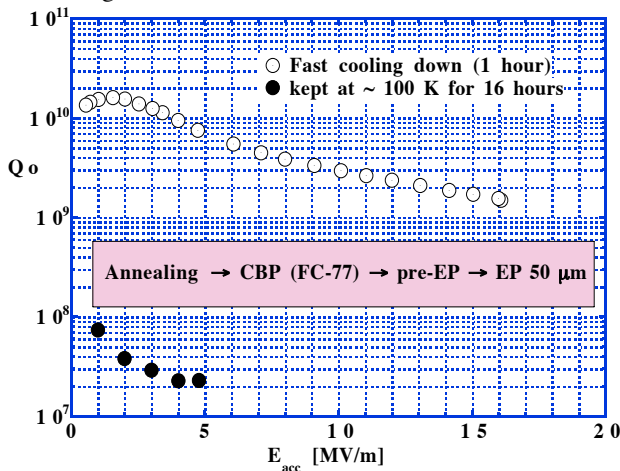

Figure 4: Heavy hydrogen Q-disease did occur when hydrogen-free CBP and EP were combined

We measured the cavity performance. The result showed a heavy hydrogen Q-disease as presented in Figure 4. As already seen in Figure 1, hydrogen Q-disease didn't occur in the case when only EP was applied to the cavity. Hence surface defects such as scratches made by the CBP are suspected to be the cause of hydrogen absorption in the following EP. To confirm this, we applied the hydrogen-free CBP to niobium samples. Then we made EP them by different removals. Hydrogen concentrations in these samples are shown in Figure 5. We thus reconfirmed that hydrogen absorption occurred during the EP process after the hydrogen-free CBP.
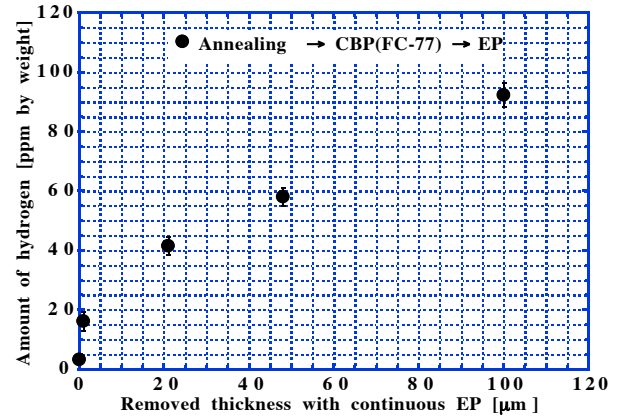

Figure 5: Hydrogen absorption occurred during EP that followed after the hydrogen-free CBP

Combination of hydrogen-free CBP and CP

To compare EP with CP, we treated a cavity with the combination of hydrogen-free CBP and CP. In this case, hydrogen Q-disease was not observed as shown in Figure 6. Consistent result was obtained by hydrogen gas analysis using niobium samples as seen in Figure 7. While the amount of hydrogen was detected to be very small, the hydrogen located near the surface. No hydrogen was observed after removing more than 20μm. Now we discovered a hydrogen-free process by the combination of the hydrogen-free CBP and CP.
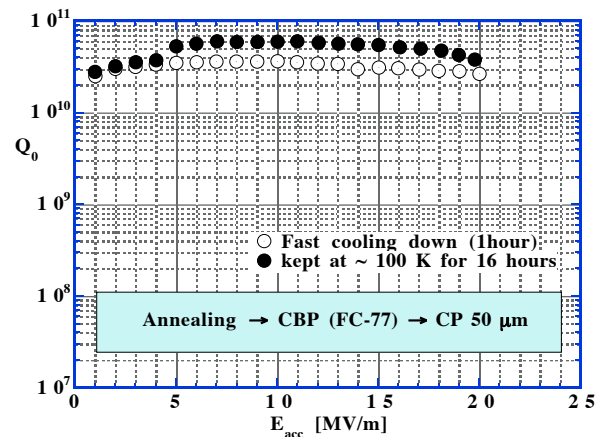

Figure 6: Hydrogen Q-disease did not occur with combination of hydrogen-free CBP and CP

The results were different between the applications of EP and CP after hydrogen-free CBP. What was the reason? Etching process in metals usually consists of the oxidation process and its dissolving process. In the case of CP, oxidation is chemically produced by the acid, while in the EP it is done electro-chemically by the applied voltage. Our EP acid for niobium consists of hydrofluoric acid and sulfuric acid. CP acid consists of hydrofluoric acid, phosphoric acid and nitric acid. Nitric acid is a powerful oxidizer. We considered that the in-situ oxidation by CP is the key. The effect of oxidation for hydrogen passivation can be seen in Table 1. When we used hydrogen peroxide instead of water in the CBP, hydrogen concentration was reduced to 1/3.
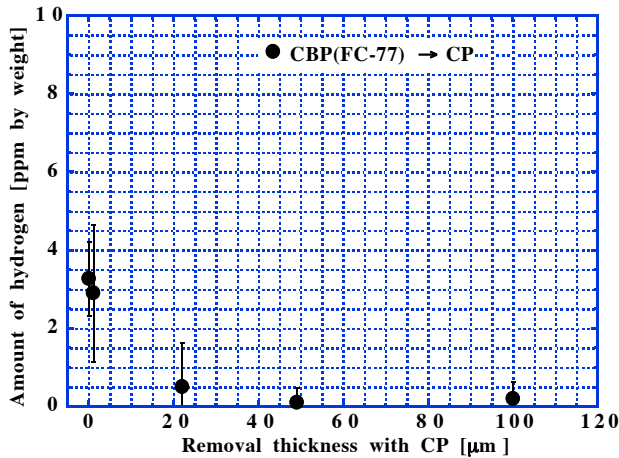
Figure 7: Hydrogen absorption did not occur during CP that followed after hydrogen-free CBP

New EP acid

We expected that adding the in-situ oxidation process is effective to reduce hydrogen absorption for EP. We had the idea to add nitric acid into the EP acid in order to prevent hydrogen absorption. Here, if the amount of nitric acid is too much, the surface by the new EP acid would be the similar surface as CP, so that cavity performance would be limited at low field due to the rough surface finishing. To know the optimum amount of added nitric acid from the finishing surface the point of view, we measured the etching speed for the several EP acids with different amounts of nitric acid. The result is in Table 2. About the case of 15000ppm nitric acid, removal thickness in an hour was 68μm by dipping and this was more than that by EP (40μm) and resulted in CP finishing. In the case of 1500ppm, it was 0.5μm, which is smaller enough than by EP and no change was observed on the surface. Hence we considered that 15000ppm of nitric acid is too much and 1500ppm is acceptable.

To find out the optimum amount of nitric acid from the passivation of hydrogen point of view, we made EP niobium samples and measured hydrogen. After hydrogen-free CBP we removed 100μm by continuous EP using new EP acids contained various proportion of added nitric acid (from 1500ppm to 15ppm). The result is

in Table 3. In the sample test, even the 15ppm of nitric acid showed passivation for the hydrogen absorption.

Table 2: Hydrogen absorption through a combination of hydrogen-free CBP and nitric acid-added EP

Concentration of nitric acid in EP acid	Removed thickness	Time of treatment	Treatment
15000 [ppm]	68 [microns]	1[hour]	Dipping (CP)
1500 [ppm]	0.5[micron]	1[hours]	Dipping (CP)
1500 [ppm]	40 [microns]	1[hours]	EP

Then we measured amount of hydrogen absorption in the pre-EP on samples using the nitric added EP acid. The result is shown in Table 4. Here, we used the EP acid repeatedly to get the 4 data by adding nitric acid in turn because each EP produced a small loading on the EP acid. From these results, we decided the optimum concentration of nitric acid as 1500ppm.

Table 3: Hydrogen absorption through a combination of hydrogen-free CBP and nitric acid-added EP

Concentration of nitric acid in EP acid	Hydrogen concentration	Removed thickness by nitric acid-added EP
15 [ppm]	1.69±0.22 [ppm]	110
150 [ppm]	1.03±0.44 [ppm]	100
1500 [ppm]	0.53±0.28 [ppm]	100

(2.5mm x 1.0mm x 147mm, RRR=200)

Table 4: Hydrogen absorption through hydrogen-free CBP and nitric acid-added pre-EP

Concentration of nitric acid in EP acid	Hydrogen concentration
0[ppm]	8.6±1.2 [ppm]
15 [ppm]	15.4±1.3 [ppm]
150 [ppm]	27.0±9.8 [ppm]
1500 [ppm]	2.8±1.8 [ppm]

(2.5mm x 1.0mm x 147mm, RRR=200)

Hence, as the next step we confirmed the combined process on the cavity: hydrogen-free CBP, pre-EP by the new acid added 1500ppm nitric acid, and 50μm EP by the conventional EP acid. We measured performance of
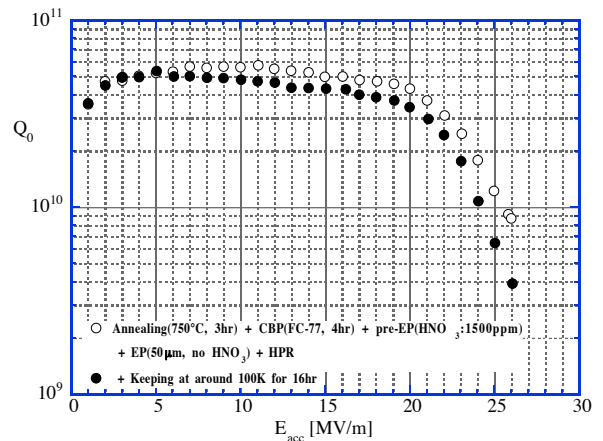

Figure 8: No hydrogen Q-disease resulted for combination of H-free CBP and oxidizer added EP

this cavity. No hydrogen Q-disease was observed and 26MV/m of accelerating gradient was achieved as shown in Figure 8. Now we have developed the hydrogen-free treatment for EP. But still the gradient was problem.

Surface Roughness and limit of accelerating gradient

Though we succeeded to develop hydrogen-free treatment, the accelerating gradient was still limited to 26MV/m. Probably the surface was too rough due to the small material removal of 50μm. We measured surface roughness of the niobium samples on which CBP was applied. As we selected polishing media GCT to get high removal rate, the roughness of finished surface was large and about 11μm in Rz (white circle of Figure 9). The additional CBP for 1 hour using another media FC also was tried and the roughness was measured (black circle of Figure 9). As shown in Figure 9, the additional CBP made the roughness 1μm smoother. After 50μm of EP, the roughness was about 6μm for the case of usual CBP (GCT media) and about 5μm for the case of the

additional CBP by FC media. To check the influence of the roughness on the high gradient, we measured cavity performance for the additional CBP with FC media. The result is shown in Figure 10. High accelerating gradient of 30MV/m was achieved without hydrogen Q-disease. To improve the gradient to 40MV/m, we have a plan to measure cavity for further smooth surface.

Discussion

Mechanism of Hydrogen Absorption

It is well known that hydrogen is more likely to be trapped on grain boundaries or dislocations in metals. Figure 11 shows images of the entrance path for hydrogen into the metal bulk [7]. Hydrogen is often trapped on dislocations and enters into the bulk through the tunnel structure (left in Figure 11). There are many dislocations and impurities at grain boundary. Grain boundary also is the trapping center. G. Katano applied tritium (isotope of hydrogen) SEM autoradiography method to search hydrogen trapped sites [7]. Beta-rays from the tritium hit photo emulsion and one can see trapped tritium location which should be very similar to hydrogen trapping. Figure 12 shows their typical study result about hydrogen trapped sites on surface of high-strength steel [7]. One can see tritium concentrating on the grain boundary (A). Another trapping center was detected in a cell (B) was
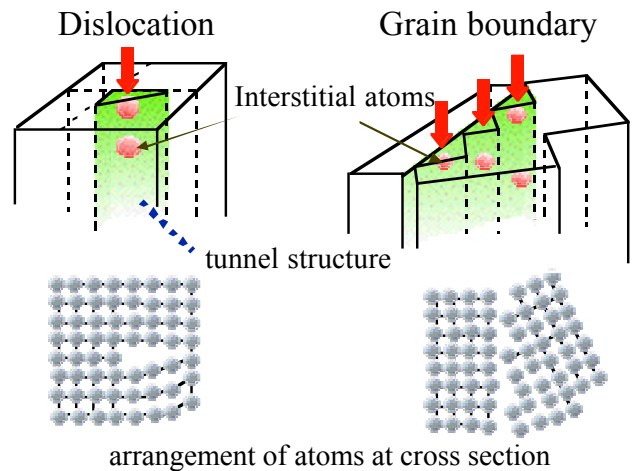

Figure 9: Surface roughness on which CBP and EP were applied

Figure 11: Hydrogen atoms entering into a material.

Figure 10: accelerating gradient of 30MV/m was achieved with a combination of hydrogen-free CBP, oxidizer added pre-EP and conventional EP
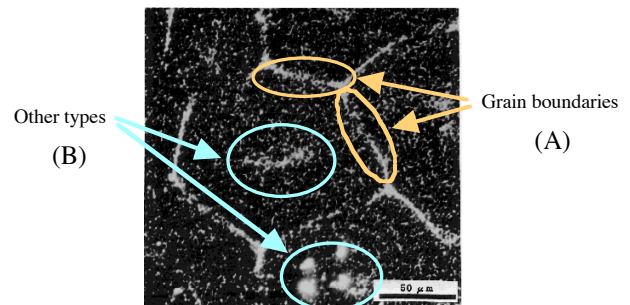

Figure 12: Tritium SEM autoradiography on high-strength steel. White spots, which are silver grains, show trapped tritium location.

observed with the method.

Our niobium surface, on which CBP was applied, has a lot of defects where dislocations concentrate. Figure 13 is a SEM image of niobium surface after hydrogen-free CBP and light EP were applied. In this case, there are a lot of small holes (arrow signs), that implies entrance paths for hydrogen.

While in the case of a combination of hydrogen-free CBP and light CP, these holes were not observed (Figure 14). Oxidized layer often appears as lighter image with SEM. Figure 14 is lighter than Figure 13. This suggests that there is oxidized layer on surface on which CP was applied. From these observations, we conclude that oxidized layer prevents hydrogen absorption.
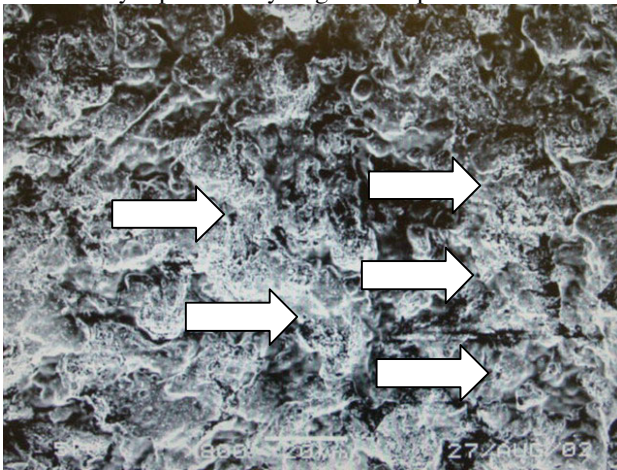
Figure 13: Hydrogen-free CBP + EP 1μm
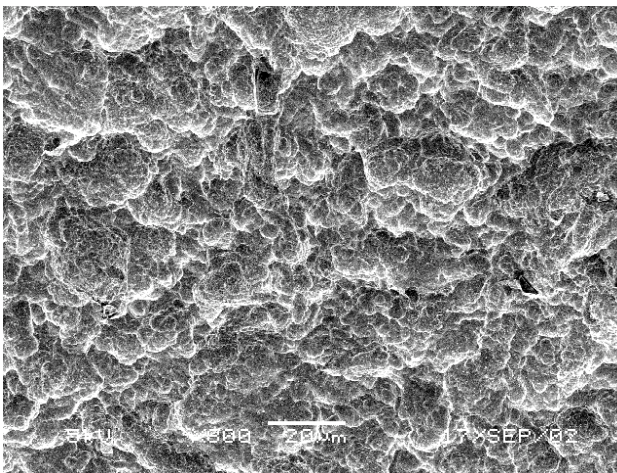
Figure 14: Hydrogen-free CBP + CP 3 μm

Cost reduction effect

As a result of this study, much cost reduction will be achieved. Figure 15 shows our estimate on the surface treatment cost for an L-band 9-cell cavity. With our new treatment process, surface treatment cost can be reduced to less than a half.

In addition, much time reduction is expected by our new surface treatment process. It takes 27 working days to treat a cavity by TRISTAN method, while our new method can be completed in 4days. For a mass production,

this time reduction leads to another much cost reduction due to less labor costs and less treatment lines.
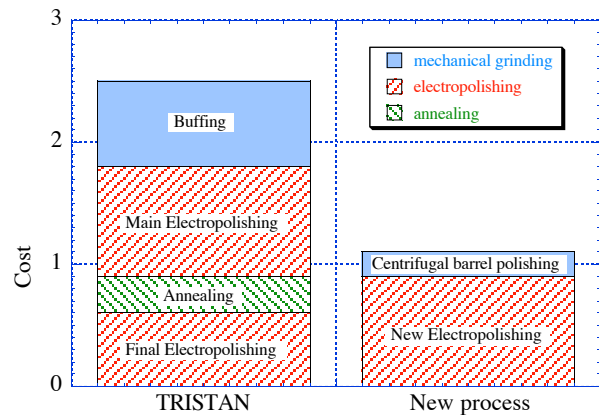

Figure 15: Surface treatment cost reduction

CONCLUSION

Our study can be summarized as follows;

1) Surface defects caused by mechanical grinding are the most likely paths for hydrogen absorption.
2) Continuous oxidization effectively prevents hydrogen absorption.
3) We innovated a Hydrogen-free mechanical grinding method (CBP) using Hydrogen-free liquid for the grinding.
4) We developed a Hydrogen-free Electropolishing by adding a little amount of oxidizer into the conventional Electropolishing solution.
5) High accelerating gradient of 30MV/m was achieved with a combination of the hydrogen-free CBP and the new Hydrogen-free Electropolishing, without annealing process. By this new method, one can simplify the process and reduce the cost dramatically.

ACKNOWLEDGMENTS

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