STUDY ON POLISHING METHOD OF Nb SURFACE BY PERIODIC REVERSE CURRENT ELECTROLYSIS WITH ALKALI SOLUTION*

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Abstract

Currently, electropolising method is thought to be the best method for the final surface preparation of superconducting RF cavity to obtain high gradient. In this conventional electropolising method, the electrolyte is the mixture of fluoric and sulfuric acids. Therefore, the operation of this method is dangerous, and the equipment becomes expensive because all parts should be made of high density polyethylene or fluorocarbon resin to avoid metallic parts which suffers from corrosion by electrolyte. Moreover, sulfur is produced as byproduct in the electropolishing process and this causes degradation of cavity performance. In order to overcome these drawbacks, we studied new polishing method of Nb surface by periodic reverse current electrolysis with alkali solution which causes no sulfur and allows the usage of metallic parts to realize cost effective equipment. In the study, we performed experiment of Nb coupons by this new method and obtained as good surface roughness as conventional electropolishing method. In this article, we report the details of the study.

INTRODUCTION

Final surface preparations of niobium (Nb) superconducting radio frequency (SRF) cavities play a critical role in order to achieve high performance of cavity. Electropolishing with sulfuric acid (H_2SO_4) and fluoric acid (HF) is thought to be the best final surface preparation method to achieve higher gradient of SRF cavity and it has already been conventional technology around the world as the standard [1]. Development of electropolishing method that does not use fluoric acid is desired in the mass-production of SRF cavities in the future project like ILC, because the electrolytic solution used in this method is very dangerous for the operator due to toxic gases (ex. H_2S, SO_x) generated in the operation and then the complex instrumentation and operation are required for the safety which increase the cost. In addition, it is reported that sulfur is produced as byproduct in the process and this causes degradation of cavity performance [2]. Equation (1) shows the chemical reaction which creates sulphur as byproduct.

$$xH_2S + SOx \rightarrow xH_2O + (x+1)S \quad (1)$$

Then the development of electropolishing method without containing sulfur is also desired. In such situation, Faraday Inc. and FNAL have studied the periodic reverse (PR) electropolishing method with diluted H_2SO_4 for the superconducting RF cavity [3]. In the PR method, the sign of applied voltage is periodically switched to positive and negative in the electropolishing process. Typical periodic reverse current in the process is shown in Fig. 1. In the plating process, this method has been widely used and applied in industries in order to obtain uniform thickness of plating.

In this paper, we report PR electropolishing method with NaOH solution. We selected NaOH as electrolyte for the following reasons. 1) If NaOH solution is used, it is possible to fabricate apparatus with metal instead of fluorine resin. 2) The NaOH solution has chemically simple composition and then it is easy to monitor the contamination and also the prediction of reaction is easy. 3) It is known that Nb and Nb oxide dissolve in NaOH solution.

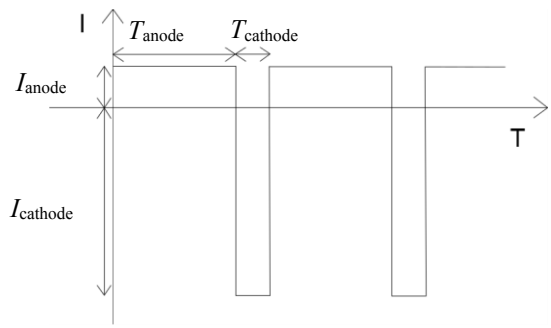

Figure 1: Typical periodic reverse current.

EXPERIMENTAL DETAIL

Experimental Setup

The experimental setup for the coupon test of PR method is shown in Fig. 2. Nb coupon is anode and Pt mesh is cathode. Specification of power source is as follows; I_{anode}=0-40 A, T_{anode}=10-99.9 ms, $I_{cathode}$=-100-0 A, $T_{cathode}$=0.1-2.0 ms. Water bath is used to control the temperature. We used EDX for the surface analysis of Nb and ICP for analysis of Nb in the solution, respectively. In addition, a laser/optical microscope is used for surface observation and a stylus-type roughness-meter is used to measure the surface roughness.

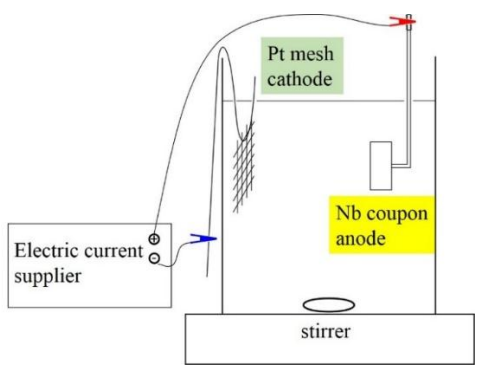

Figure 2: Schematic of the experimental apparatus.

Preparation of Nb Coupon

The Nb coupon (10 mm x 10 mm x 2 mm) was masked with polyethylene in order to obtain controlled exposure of surface as shown in Fig. 3. The Nb coupon is contacted with Fe cube (8 mm x 8 mm x 10 mm) and both the Nb coupon and the Fe cube are moulded in polyethylene. A screw hole was made on the backside of Fe cube to connect the stainless steel (SUS304) rod which is covered by the tape of fluorine resin. Nb surface was polished with #1000 sandpaper in order to prepare flat and uniform surface of Nb coupon. Abrasive particles on the surface due to the polishing were removed by buffered chemical polishing with the solution in the component ratio of H_3PO_4 : HNO_3 : HF = 1 : 1 : 1. The measured roughness of Nb surface was Ry=2.3 μm (JIS'94) after the preparation process.

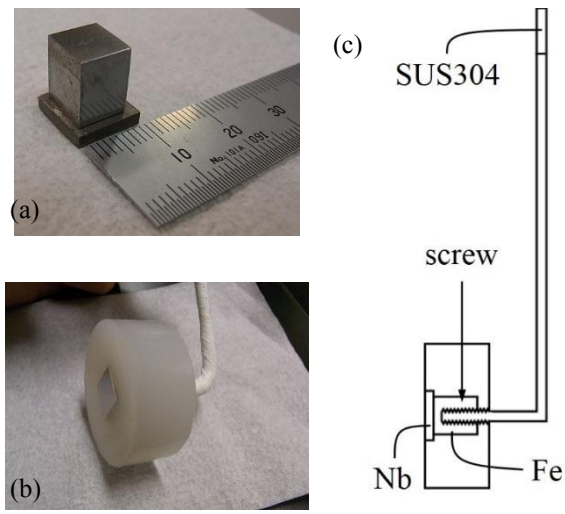

Figure 3: (a) Nb coupon (10 mm x 10 mm x 2 mm) and Fe cube (8 mm x 8 mm x 10 mm). (b) Nb coupon and Fe cube are masked by polyethylene. (c) Schematic of Nb anode with stainless steel (SUS304) rod.

EXPERIMENTAL RESULTS

Experiments with Various Acids

We firstly performed the experiment with the solution of H_2SO_4. Nb coupon was electropolished with PR current (T_{anode}=10 ms, I_{anode}=+0.6 A, $T_{cathode}$=2 ms, $I_{cathode}$=-2.4 A) for 30 minutes in 10 v/v% H_2SO_4 solution at room temperature. The picture of Nb coupon during the experiment is shown in Fig. 4. Black particles are generated from the Nb surface with gases. A metallic glossy surface of Nb coupon was observed after the process, which is found to be the surface with a micro structure in the size of about 20 μm from the observation by a laser/optical microscope. The surface roughness was measured to be Ry=2.1 μm. Since Nb was detected from the solution by the analysis with ICP, we considered that the black particles might be substances derived from Nb coupon. By this observation, we thought Nb oxide made by electric oxidation might be desorbed, not ionized in H_2SO_4 solution. In addition, no precipitate was observed in H_2SO_4 solution.

Figure 4: Electrolysis in H_2SO_4 solution.

We also tried electropolishing by the same setup with various solutions: hydrochloric acid (HCl), nitric acid (HNO_3), and phosphoric acid (H_3PO_4). Results of experiments with HCl and HNO_3 were similar to that of H_2SO_4. In an experiment with H_3PO_4, the surface of Nb coupon exhibited a rainbow color in the region of high current density where the Nb oxide thin film of gradual thickness might be formed. Fig. 5 shows the pictures of Nb coupon surfaces after the experiments with various solutions.

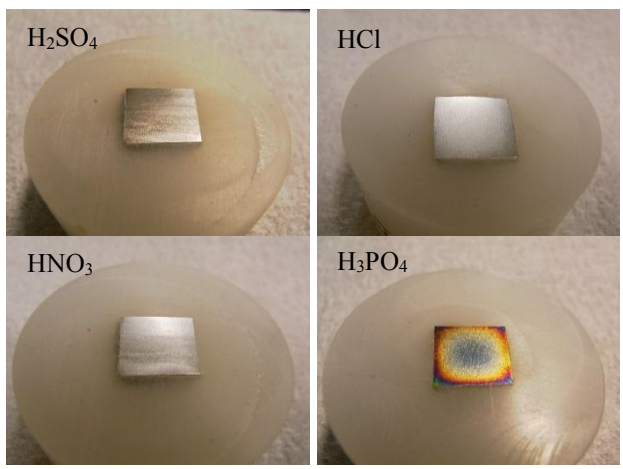

Figure 5: Comparison of surfaces polished with various acids by periodic reverse current electrolysis.

Experiment with NaOH Solution

Nb coupon was electropolished with PR current (T_{anode}=2 ms, I_{anode}=-2.4 A, $T_{cathode}$=10 ms, $I_{cathode}$=+0.6 A) for 30 minutes in 100 g/L NaOH solution at room temperature. Nb surface became brown and gas was generated by electric current. Continuing the experiment for a while, a brown film peeled from the Nb surface. The brown film hanging on the surface of Nb coupon in the electropolishing is shown in Fig 6. The surface with a metallic glossy appeared after washing with water. A micro structure in the size of about 15 μm was observed on the Nb coupon by a laser/optical microscope. The surface roughness was measured to be Ry=1.5 μm. Fractions of the brown film were suspending after the electropolishing in NaOH solution. All the fractions of

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film changed into white powder and after a while they precipitated at the bottom of the bath. We analyzed the white powder in the NaOH solution by EDX and it was found that the white powder includes Nb.

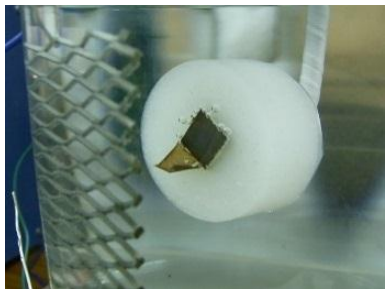

Figure 6: Brown film on the Nb coupon in the Eelectrolysis with NaOH solution.

Parameter Search

Experiments with the same setup were conducted repetitively by changing the current waveforms, NaOH concentrations, solution temperatures, and time durations. As the result, we found followings. 1) The greater the amount of gas generated on electrode is, easier the film peels. 2) The film production rate depends on electric current rate. 3) The dissolution reaction depends on the concentration and temperature of NaOH solution. Therefore, the balance of oxidation and dissolution is very important for surface finishing. The condition for the best smooth surface of Nb coupon was as follows; T_{anode}=10 ms, I_{anode}=+0.6 A, $T_{cathode}$=2 ms, $I_{cathode}$=-2.4 A, temperature = 50ºC, NaOH concentration = 100 g/L, polishing time duration = 30 minutes.

We also performed experiments of electropolishng with a simple setup with samples of Nb plate as the anode. We compared the surface of Nb plate samples which were electropolished with NaOH and H_2SO_4 solutions. There was no significant difference on the surface finishing and both surfaces had similar micro structures and appearances. But the surface roughness polished with NaOH solution was slightly better than that polished with H_2SO_4 as shown in Fig 7.

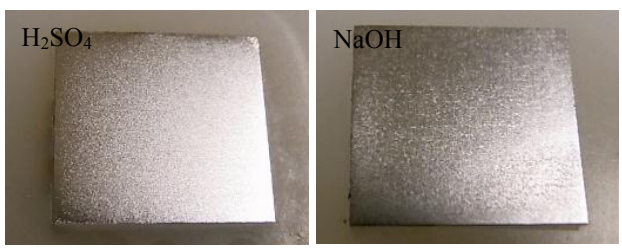

Figure 7: Comparison of the surface of Nb plates by electropolishing with H_2SO_4 and NaOH solutions.

DISCUSSIONS

In the electropolishing process with NaOH solution, brown film was produced continuously on the Nb coupon. It was revealed that white powder observed in NaOH solution includes Nb from EDX analysis. We considered that the white powder might be $NaNbO_3$, since Nb might form NbO_3^- in basic aqueous solution [4]. If the brown film is assumed to be Nb oxide, Nb oxide might be formed by electrical oxidation in a film shape and it dropped out by gas generation from the Nb surface. And then it might become $NaNbO_3$ by reaction with NaOH. The considered reaction is described below.

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 5H_2 + 10e^- \quad (2)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (3)$$

$$Nb_2O_5 + 2NaOH \rightarrow 2NaNbO_3 + H_2O \quad (4)$$

CONCLUSION

We electropolished Nb coupons with various acids of solution including NaOH and H_2SO_4 by applying PR current. The surface roughness by electropolishing with H_2SO_4 solution was Ry=2.1 μm. On the other hand, it was Ry=1.5 mm by electropolishing with NaOH solution. As the results of parameter search, the best condition in the series of experiments for the smooth surface of Nb coupon was as follows; T_{anode}=10 ms, I_{anode}=+0.6 A, $T_{cathode}$=2 ms, $I_{cathode}$=-2.4 A, temperature = 50ºC, NaOH concentration = 100 g/L, polishing time duration = 30 minutes.

REFERENCES

[1] S. Noguchi et al., JPN Patent 1999350200.
[2] F. Furuta et al., The 5th Annual Meeting of Particle Accelerator Society of Japan and 33rd Linear Accelerator Meeting in Japan, August 6-8, 2008, Higashihiroshima, Japan, p827-829.
[3] E.J. Taylor et al., US Patent 2014/0018244 A1.
[4] George Calota, Natalia Maximova, Katherine S. Ziemer, and Sinan Müftü (2009), “Investigation of Chemical/Mechanical Polishing of Niobium”, Tribology Transactions, 52, 4, p447-459.