

STUDY ON ELECTRO-POLISHING OF NB SURFACE BY PERIODIC REVERSE CURRENT METHOD WITH SODIUM HYDROXIDE SOLUTION

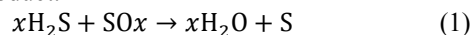
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Abstract

Electropolishing (EP) is one of the best methods of Nb surface finishing of the superconducting cavity to obtain high accelerating gradient. In the EP process, mixed solution of hydrofluoric acid and sulfuric acid is generally used. But this solution is very dangerous in the operation. Furthermore, all equipment must be made of high density polyethylene or fluorocarbon resin because the corrosion of the metal occurs by hydrofluoric acid. These are the reasons why the cost of EP process and instrument become very expensive. In addition, this solution produces sulfur compound on the Nb surface in the EP reaction. This sulfur compound can be field-emission sources on the inner surface of cavity and degrades acceleration performance. In this article, we report a novel EP method using periodic reverse current and sodium hydroxide solution. The reaction produces no sulfur content and the equipment is less expensive because the instrument can be made of usual plastic material. As the result of experiments with Nb-coupon samples, we found that the surface roughness is equivalent to the conventional EP method.

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 (H₂SO₄) 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. HF, H₂S, 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 by-product.



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 (EP) method with diluted H₂SO₄ for the superconducting RF cavity [3]. In the PR-EP method, the sign of applied voltage is periodically switched to

positive and negative in the EP process. Typical periodic reverse (PR) current 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-EP 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 and/or usual plastic material 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. 4) Degreasing effect is expected with NaOH solution. This might omit the degreasing process after EP process. The first report of studies on PR-EP method with NaOH solution is found elsewhere [4].

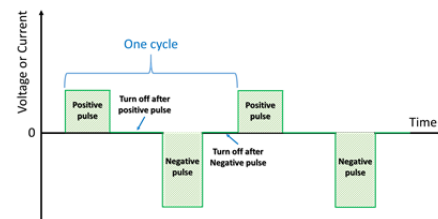


Figure 1: Typical wave form of periodic reverse current.

We studied following subjects for the PR-EP process:

- Parameter search for smooth Nb surface and study about pulse-shape dependence in the creation of oxidation film.
- Chronopotentiometry measurements.
- Component analysis of generated gas.

PARAMETER SEARCH

We performed Nb-coupon experiments for PR-EP method both at Jefferson Laboratory and Nomura Plating Co., Ltd. The experimental setups are shown in Fig. 2, where Fig. 2 (a) shows a setup at Jefferson Laboratory, Fig. 2 (b) shows one at Nomura Plating Co., Ltd and Fig. 2 (c) shows schematic illustration of setup. As shown in Fig. 2 (c) Nb coupon is anode and Pt mesh is cathode. Periodic Reverse (PR) voltage is applied between anode and cathode.

We performed several PR-EP experiments with various wave forms for sulfuric acid and alkaline solutions. Table 1 shows typical parameter sets (No. 1 – 6) in the experiments. Experiments of parameter set No.1 and No.2 were performed at Jefferson Laboratory. Experiments of the

rest of parameter sets were performed at Nomura Plating Co., Ltd. Fig. 3 shows the pictures and surface roughness (Ry) of Nb-coupon samples before and after PR-EP processes. Fig. 3 also shows that the parameter set No. 6 gave the smoothest surface roughness (Ry) of 1.6 μm .

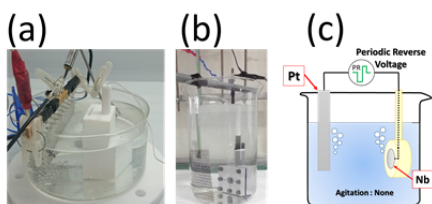


Figure 2: Experimental setup. (a) A setup at Jefferson Laboratory, (b) a setup at Nomura Plating Co., Ltd, and (c) schematic illustration of setup.

	picture	Roughness (Ry) [μm]	picture	Roughness (Ry) [μm]
(a) Parameter set No. 1	Before EP	NA	Before EP	NA
	After EP	NA	After EP	NA
(b) Parameter set No. 2	Before EP	NA	Before EP	NA
	After EP	NA	After EP	NA
(c) Parameter set No. 3	Before EP	3.8	Before EP	3.5
	After EP	5.4	After EP	2.0
(d) Parameter set No. 4	Before EP	5.1	Before EP	3.8
	After EP	2.5	After EP	1.6
(e) Parameter set No. 5	Before EP	5.1	Before EP	3.8
	After EP	2.5	After EP	1.6
(f) Parameter set No. 6	Before EP	5.1	Before EP	3.8
	After EP	2.5	After EP	1.6

Figure 3: Pictures and surface roughness (Ry) of Nb-coupon samples before and after EP processes.

In the next step we studied pulse-shape dependence in the creation of oxidation film. In the study parameter set No. 2 was used as starting reference. Positive-pulse voltage was fixed at 3 V. Turn off times after positive and negative pulses were fixed to 0 and 5 ms, respectively. Because the wave form of positive current corresponds to oxidation process on Nb-coupon sample, we observed the wave form of positive current with changing positive-pulse width, negative-pulse width, and negative-pulse voltage. Fig. 4 shows the results of study. Fig. 4 (a) is for the width of positive pulse: 2.5 ms, (b) is for the width of positive pulse: 5.0 ms, and (c) is for the width of positive pulse: 10 ms.

positive pulse: 5.0 ms, and (c) is for the width of positive pulse: 10 ms. It was found that the wave form of positive current which correspond to oxidation process on Nb-coupon sample depends on the width of positive pulse. Shorter width of positive pulse gave longer period of positive-current wave form which corresponds to longer oxidation process. If short and low negative pulse was applied, less oxidation film was created. In addition experiments were performed with various temperatures. Minor dependence on temperature was observed.

Parameter set No. 2 is used as starting reference.

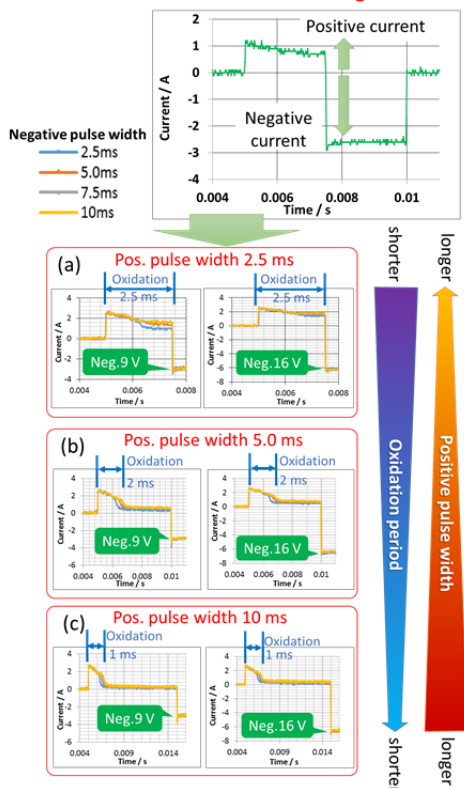


Figure 4: Positive-current wave forms for various parameters. Positive-current wave forms which correspond to oxidation process on Nb sample depends mainly on the width of positive pulse. (a) Width of positive pulse: 2.5 ms, (b) width of positive pulse: 5.0 ms, and (c) width of positive pulse: 10 ms.

Table 1: Parameter Sets in PR-EP Experiments

Parameter set No.	1	2	3	4	5	6
Solution	H_2SO_4 37%	NaOH 30%	H_2SO_4 50%	NaOH 10%	NaOH 10%	NaOH 10%
		$(\text{COOH})_2$ 0.05%		$(\text{COOH})_2$ 0.05%	$(\text{COOH})_2$ 0.05%	$(\text{COOH})_2$ 0.05%
Temperature	20	50	20	20	50	50
PR wave form positive pulse	Voltage [V]	3				
	Pulse width [ms]	2.5	2.5	3	3	3
	Turn off time [ms]	1	0	0	0	0
PR wave form negative pulse	Voltage [V]	9				
	Pulse width [ms]	2.5	2.5	3	3	3
	Turn off time [ms]	0	5	5	5	5

CHRONOPOTENTIOMETRY MEASUREMENT

In order to study the process of oxidation-film creation during positive-voltage pulse, chronopotentiometry measurement was performed. Fig. 5 (a) shows the experimental setup. Potential of Nb-coupon surface was measured between Nb and reference electrodes with applying constant current from Nb-coupon to Pt electrode for 100 s and turning off the current. The solution was alkaline at the temperature of 20 °C. Fig. 5 (b) shows the resultant plot.

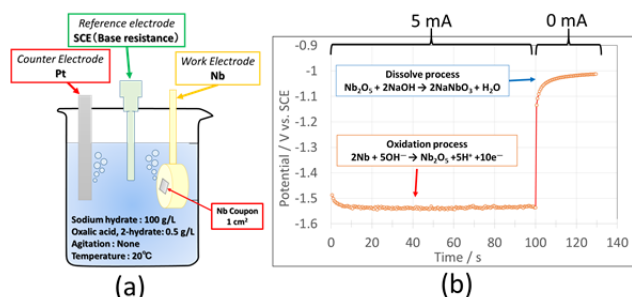


Figure 5: (a) Experimental setup. (b) Nb surface potential (vs. SCE) vs. time.

COMPONENT ANALYSIS OF GENERATED GAS

In order to understand reactions on each electrode, generated gas was analysed on both electrodes. Fig. 6 shows the experimental setup. Parameter set No. 6 was used for

the wave form. Positive pulse (voltage = 3 V, width = 3 ms, $T_{\text{off}} = 5$ ms) and negative pulse (voltage = 9 V, width = 3 ms, $T_{\text{off}} = 5$ ms) were applied for sulfuric acid and alkaline solutions with changing temperature.

More gas was generated for alkaline solution than sulfuric acid solution. In particular, enormous amount of gas was generated for alkaline solution at 50 °C. Gas analysis was done by gas-detecting tube as shown in Fig. 6 and the results are shown in Table 2. It was found that on the Nb electrode the process of oxidation-film creation is dominating and reduction reaction of NaOH solution is suppressed. It was also found that on the Pt electrode reduction reaction of NaOH solution is dominating and electrolysis reaction is suppressed.

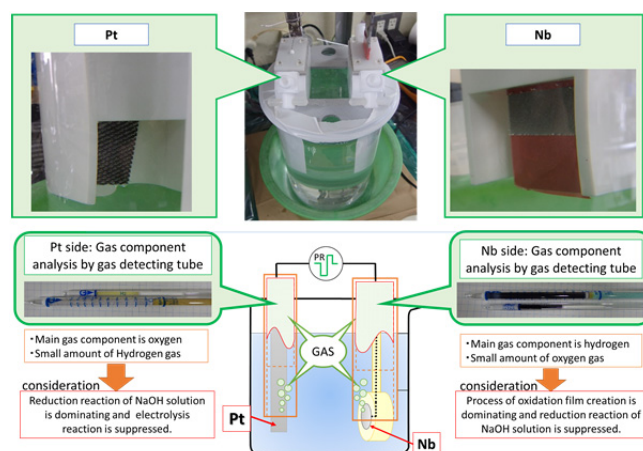


Figure 6: Experimental setup for gas analysis.

Table 2: Results of Gas Analysis

Solution	H ₂ SO ₄ 50%		NaOH 10%		NaOH 10%	
			(COOH) ₂ 0.05%		(COOH) ₂ 0.05%	
Temperature [°C]	20		20		50	
Gas	O ₂	H ₂	O ₂	H ₂	O ₂	H ₂
Nb	No detection	Detected (>2%)	Detected (<6%)	Detected (>2%)	Detected (<6%)	Detected (>2%)
Pt	Detected (>24%)	No detection	Detected (>24%)	No detection	Detected (>24%)	No detection

SUMMARY

The parameter set for smooth Nb surface (Roughness $R_y = 1.6$ μm) was found in PR-EP with alkaline solution. We studied pulse-shape dependence in the creation of oxidation film. Shorter width of positive pulse gave longer period of positive-current wave form for oxidation process. In order to understand reactions on each electrode, generated gas was analysed on both electrodes. More gas was generated for alkaline solution than sulfuric acid solution. It was found that on the Nb electrode the process of oxidation-film creation is dominating and reduction reaction of NaOH solution is suppressed. It was also found that on the Pt electrode reduction reaction of NaOH solution is dominating and electrolysis reaction is suppressed.

ACKNOWLEDGEMENT

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