

ALTERNATE ELECTROLYTE COMPOSITION FOR ELECTROPOLISHING OF NIOBIUM SURFACES*

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Abstract

Electropolishing has shown promising results for the treatment of Nb cavities to be used in particle accelerators, particularly in the attainment of high surface electric fields. In support of the CEBAF Upgrade project and as part of a longer-term R&D program we have investigated the properties of several electrolyte recipes. A particularly promising one consists of a mixture of lactic, sulfuric, and hydrofluoric acids. Initial tests reveal that smooth Nb surfaces can be achieved with no observable grain boundaries under optical microscope. We report on the results of the investigations of the parameters that control the polishing process using this particular acid mixture.

1 INTRODUCTION

Electropolishing has been a standard technique widely used in industry to obtain smooth and lustrous surface finish on various metals. Smoothing is achieved due to the dissolution of surface metal away from the bulk according to Faraday's law, which takes place preferentially at convex locations of a metal surface. A bright metal surface can be obtained if all the extremely fine surface asperities that causes dullness by scattering visible light is removed. Although electropolishing always was part of the surface preparation techniques available to the superconductivity radio frequency (SRF) community, there was a sharp increase of interest following the investigations that took place at KEK [1]. Since then, tremendous progress has been made in this area, as one can see from the proceedings of SRF workshops. However, to the best of our knowledge, all the reported electropolishing on Nb SRF cavities has been done using exactly the same electrolyte recipe firstly used by Diepers et al. [2] and subsequently adopted by Saito et al. [1].

To explore other alternatives, we have done electropolishing on Nb using various recipes including the one used by KEK. One particular recipe, consisting of appropriate mixture of lactic, sulfuric, and hydrofluoric acids, has shown very encouraging results in terms of surface smoothness. This type of acid mixture for electropolishing on Nb was first briefly described [3] by Monti in a French journal *Métaux Corrosion Industries* in 1958, although the ratio of the mixture described there is

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not the same as the one adopted here. In this paper, we report the results of the investigations on the parameters that control the polishing process using this particular recipe. The relationship between current density vs. applied voltage during polishing, the dependence on the distance between anode and cathode, the effect of cathode material on the finish of the polished Nb surfaces, and the effect of polishing time are studied. Optimized process is established through inspection of the polished surfaces of Nb samples using appropriate microscopic tools. We also report here the results of our initial attempts to electropolish half and single cell Nb cavities using this particular acid mixture.

2 EXPERIMENTAL

Our motivation for designing an experimental set-up for electropolishing on Nb is to try to avoid using Nb cavities as samples, since it is too costly. We believe that optimal polishing conditions can be obtained by working on small Nb samples.

Before trying to electropolish on Nb cavities, we need to know the following three parameters: a) limiting current density, b) polishing rate, and c) cathode material. A determination of the limiting current density is important, if current density is selected to be the controlling factor for electropolishing. The other alternative is voltage control. We decided to try current control first, because it has been concluded by KEK [1] that current density is a more relevant parameter. It is well established [4] now that a clean Nb surface can be obtained only after the removal of a surface layer of thickness of about 100 μm for a newly fabricated cavity. Generally speaking, this process will enable us to remove any effect from previous treatments. To minimize unnecessary electropolishing time, we need to know the polishing rate at optimal polishing conditions. One of the requirements for electropolishing is that the cathode should not react with the electrolyte. In Monti's paper [3] platinum was selected as the cathode material due to the inertness of platinum. However, platinum is very expensive. We noticed that pure aluminum is not reactive [1] with the mixture of hydrofluoric and sulfuric acids, although reactions do take place when pure aluminum is in contact with each one of the acids. This fact motivates us to find alternative materials for the cathode. We intended to try pure aluminum, stainless steel, gold plated aluminum, and platinum plated aluminum.

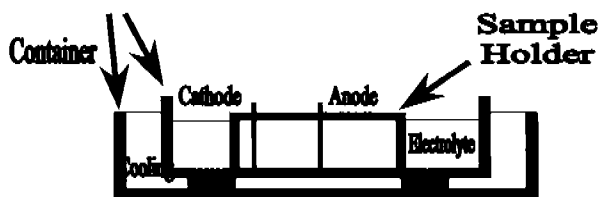


Fig.1: Schematic cross-section of the electropolishing system.

Several systems have been designed and set up to study the polishing process. One typical simple and useful system is schematically illustrated in Fig.1. Samples with dimension of $40 \times 110 \text{ mm}^3$ were sheared from a 3 mm niobium sheet. The sample holder had nine slots. The separation between each slot was 25 mm. Cathode of the same dimension was placed at one end. Therefore the longest distance between cathode and anode was 200 mm corresponding to the largest radius of a practical cavity. Cooling of the electrolyte turned out to be necessary because of the heat generated during polishing, especially when a large current density was required. This was done by filling the outer container with cooling fluid, and kept the cooling fluid flowing all the time during the polishing. In this way, we were able to keep temperature of the electrolyte below about 30°C . The length of sample or cathode immersed inside the electrolyte was 90 mm.

Before electropolishing, all samples were first cleaned using acetone and then isopropyl alcohol and subsequently by ultrasonic cleaning using de-ionized water. Finally dry nitrogen gas was used to blow away the remaining water on sample surfaces.

3 RESULTS AND DISCUSSION

Generally speaking, any electropolishing process can be characterized by plotting its anode current density (I_d) against its voltage (V) drop between cathode and anode. The detailed shape of each I_d vs. V curve depends on the configuration of each polishing set-up and is largely influenced by the distance between cathode and anode. We felt that it was less economic to study the polishing process by going through I_d vs. V curves for all different distances between cathode and anode in our set-up. Instead, we chose the middle distance as a typical one to be studied in detail, then we used the established limiting current density to study the effect of the distance between cathode and anode on the surface finish of a Nb sample.

3.1 Limiting Current Density

Normally, a typical I_d vs. V curve contains two peaks followed by a plateau and then a rapid increase of I_d with V. A sample may experience: etching, periodic oscillation of anode current density, polishing, gas evolution on the anode surface, and finally the occurrence of a comparable amount of etching and polishing. The optimum polishing conditions are located right at the transition point between the plateau area and the rapid increase of I_d with V.

Fig.2 shows a measured I_d vs. V curve for the samples being placed at the middle location of the sample holder.

We did not see the expected two peaks, but only one peak. In the vicinity of the peak, a periodic oscillation of anode current was observed. This I_d vs. V curve was reproduced more than one time, indicating therefore it was an intrinsic property of the electropolishing process for the configuration.

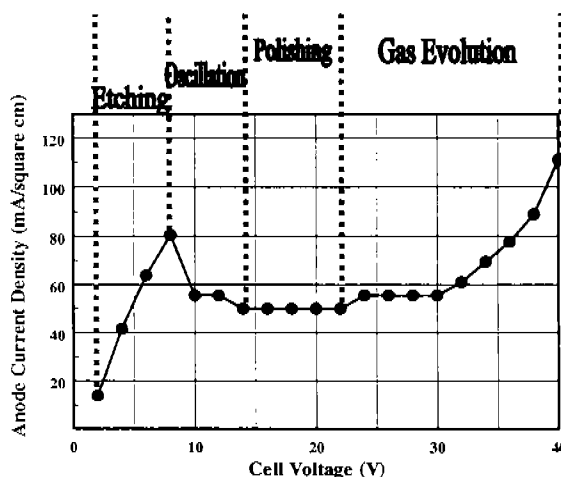


Fig.2: Anode current density measured as a function of applied voltage for the polishing system shown in Fig.1. Four areas are identified (see text for more details).

Fig.2 can also be divided into four regions corresponding to etching, periodic oscillation of anode current density, polishing, and gas evolution on the anode surface as indicated. The comparable amount of etching and polishing process was not observed up to the maximum applied voltage of 40 V. The optimum polishing conditions were, therefore, identified as a cell voltage of 23 V and an anode current density of 50 mA/cm^2 . Since we are going to use current density as the control parameter for polishing, we can discard the voltage. This optimum current density is almost the same as that for the acid mixture used by KEK [1]. The difference is that we find the occurrence of current oscillation before polishing which is opposite to that found [1] by KEK. Sometimes, we did find a slow oscillation of current taking place after the polishing region. The oscillation region was confined to a narrow voltage region from about 24 to 26 V. However, this was not reproducible and seemed to occur only when the electrolyte temperature was allowed to rise to 55°C .

Fig.3 shows how surfaces look under an optical microscope for samples from each region after electropolishing for half an hour. In the etching region, the surface morphology is almost identical to that of a sample treated by Buffered Chemical Polishing (BCP) (see Fig.4), except that in Fig.4 various surface contaminants are present, which are not seen in Fig.3a. Nb surfaces in this region appear to be very rough. The roughness is due to the enhanced etching near grain boundaries, which is, in fact, the major drawback [5] of BCP. Surfaces tend to become brighter and smoother in the oscillation region as shown in Fig.3b. Although grain

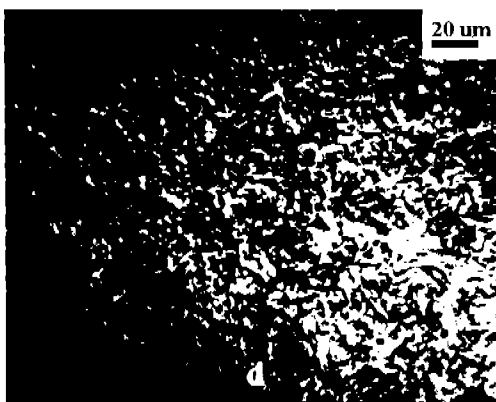
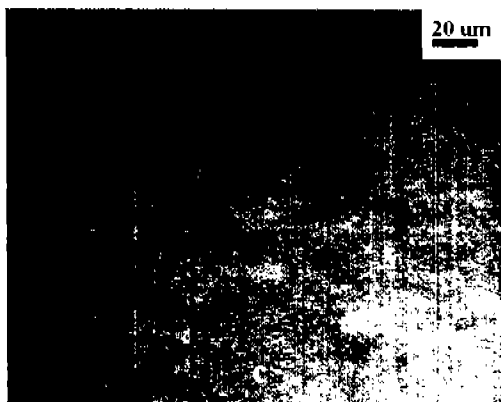
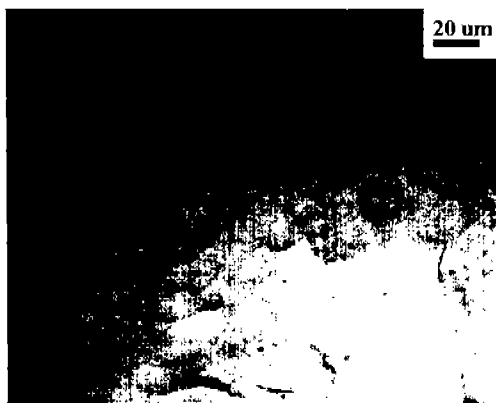


Fig.3: Typical optical images of Nb surfaces for samples treated under the conditions corresponding to the following different areas identified in Fig.2: a) etching area; b) oscillation area; c) polishing area; and d) gas evolution area.

boundaries are still visible in this region, they are not as sharp as those in the etching region, indicating therefore that electropolishing does take place in this region. In the polishing region, very smooth surfaces with no observable

grain boundaries are seen under optical microscope as shown in Fig.3c. However, the surfaces are less shiny than the surfaces of samples from the oscillation region. Finally, in the gas evolution region, pitting occurs. The typical size of the pits is about 4 μm. The sizes of the pits increase with the increasing voltage up to a typical size



Fig.4: Typical optical image of a Nb surface treated by buffered chemical polishing. Black arrows indicate some precipitates gathered at grain boundaries. White arrows show other defects observed on the surface.



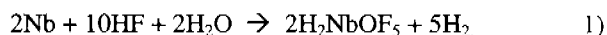
Fig.5: Typical image of a Nb surface treated under the conditions located in the extreme end point of the gas evolution region of Fig.2.

larger than 20 μm (see Fig.5). We believe that the pits are created due mainly to the generation of oxygen gas on the surface of the anode.

3.2 Polishing Rate

After the determination of the optimum polishing conditions, especially the limiting current density, we would like to know the polishing rate under such condition for a sample (anode) located in the middle slot of the sample holder. The samples were weighed before and after polishing. The mass dissolved in one hour is 1.209 g. Since the density of Nb is 8.66 g/cm^3 , the polishing rate is therefore about 0.646 $\mu\text{m}/\text{min}$. This value is much larger than 0.381 $\mu\text{m}/\text{min}$ adopted by KEK for their electrolytic recipe. The difference here is surely attributable to the different electrolytic recipes employed for polishing.

In the present recipe lactic acid is added to the mixture of sulfuric and hydrofluoric acids. The addition of an organic acid is generally believed [6] to act in the following three beneficial ways: a) it will enable electropolishing to be done at a lower anode current density and temperature; b) it can extend the useful life of the acid mixture; c) it can assist throwing power during electropolishing. Therefore, it is natural to think that the observed quicker polishing rate here is mainly a result of the addition of lactic acid to the electrolyte. Another plausible reason is due to the difference in the amount of hydrofluoric acid in the two different electrolytes. It has been known for quite a long time that in electropolishing on Nb using the mixture of sulfuric and hydrofluoric acids, the following chemical reaction takes place [7]:



This equation indicates clearly that hydrofluoric acid is the major determinative chemical compound in the electrolyte during electropolishing. We believe that equation 1 is applicable not only for electropolishing using KEK recipe, but also for that using the present electrolytic recipe. If this is true, then it is clear that the quicker polishing rate here may also be a result of larger amount of hydrofluoric acid adopted in the present electrolytic acid. The third reason may be due to the acceleration of Nb removal rate when the concentration of sulfuric acid is decreased. The last point will be also discussed in Section 3.4 later.

Fig.6 shows typical optical images of the surfaces after electropolishing for 15 and 60 minutes. They are almost identical as that after electropolishing for 30 minutes (see Fig.3c), implying therefore that polishing may take place homogeneously over the time after establishing polishing conditions. We found that the polishing conditions could be established in a time period less than two minutes.

The higher polishing rate here is beneficial to us from economic point of view. This means that it takes only 155 minutes to remove a thickness of 100 μm from a surface of Nb, which reduces the polishing time by 107 minutes

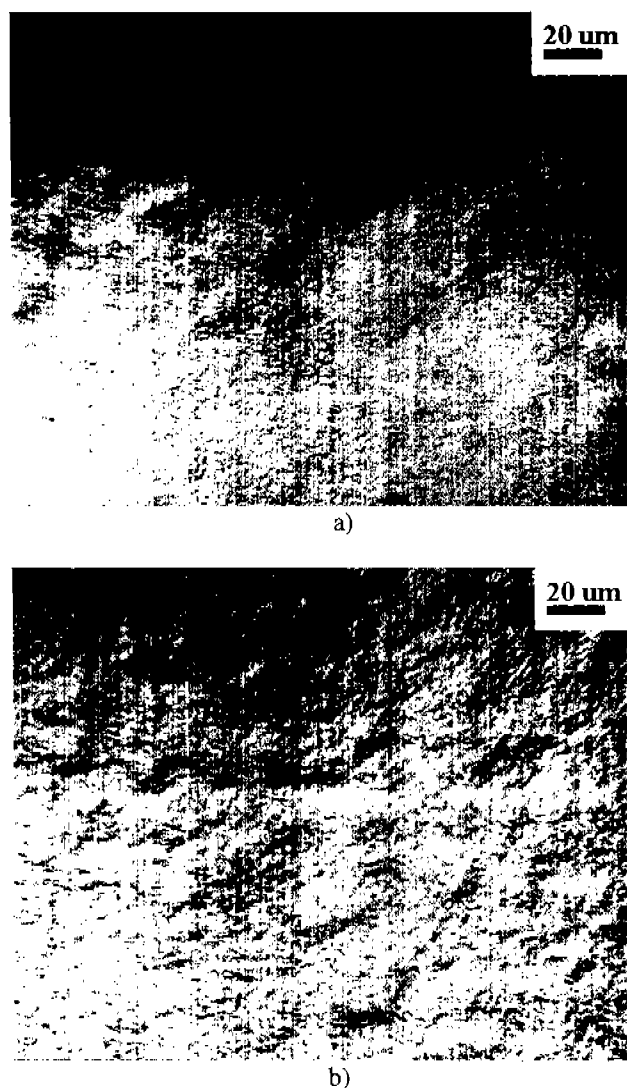


Fig.6: Typical images of the Nb surfaces treated under the application of the determined limiting current density (see text for details) for a) 15 minutes and b) 60 minutes.

as compared with that using the KEK recipe. This will result in a huge capital saving for the cost of electropolishing on Nb cavities.

3.3 Distance Effect Between Cathode and Anode

In the set-up of the electropolishing system designed by KEK, the shape of cathode is a rod. The distance between cathode and anode, therefore, varies continuously from iris to equator for a Nb cavity in that case. Intuitively speaking, the change in distance may create an inhomogeneous electric field distribution over the interior surface of the cavity, resulting in an inhomogeneous polishing. This is not good for Nb cavities, since the performance of a Nb cavity is determined by the weakest part of the cavity. If we are going to use a cathode of the same shape, we need to know how the variation in the distance affects the polishing results.

To study this effect, we first measured voltage as a function of the distance between cathode and anode when

the anode current density is fixed at 50 mA/cm^2 . The result is shown in Fig.7. It is interesting to see that the variation in voltage is only about 8% for the change of the distance from 100 to 200 mm. This implies that in this region, the major voltage drop is around the surface of Nb. Therefore the variation of the distance between cathode and anode may not be a very important parameter in this distance region.

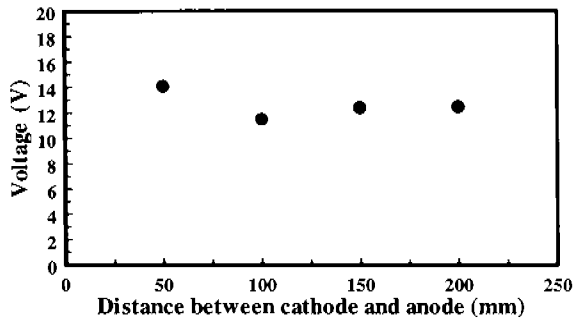
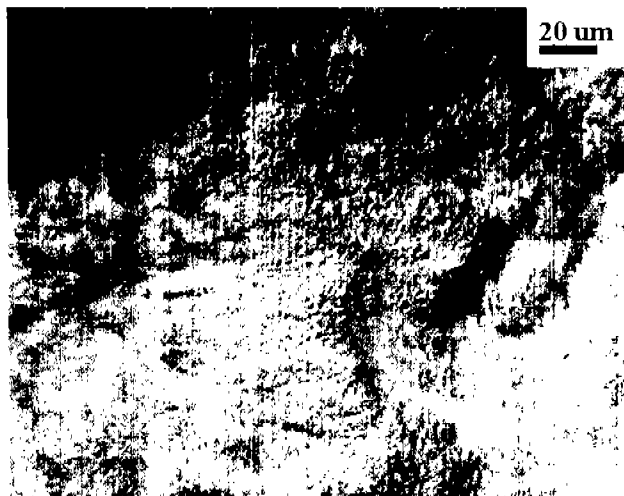


Fig.7: Voltage required to reach an anode current density of 50 mA/cm^2 for samples located at various distances away from cathode.

The surface finish for samples located at 25 and 200 mm away from cathode is examined under an optical microscope after electropolishing for half an hour at an anode current density of 50 mA/cm^2 . Typical images are shown in Fig.8. Surfaces appear to be more or less the same as that at the middle slot. This result tells us that if we are able to make sure that current density is the same everywhere on the interior surface of a multiple cell cavity a homogenous electropolishing over the whole cavity can then be achieved for a largest cavity available in practice.

We also studied the voltage variation as a function of the distance from anode when the anode current density was fixed to be 50 mA/cm^2 and the distance between cathode and anode is fixed to be 310 mm. The result is shown in Fig.9. It was hoped that such measurements would tell us whether the major voltage drop occurs near



a)

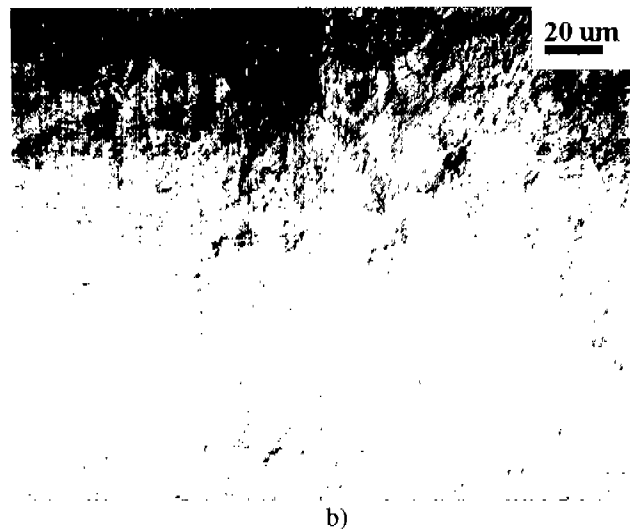


Fig.8: Typical optical images of Nb surfaces of the samples located at a) 25 mm and b) 200 mm away from cathode.

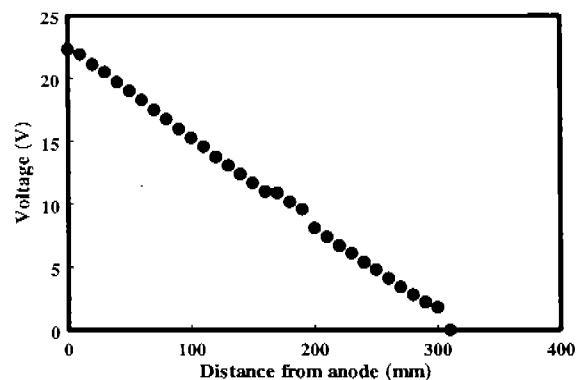


Fig.9: Variation of voltage in the electrolyte as a function of the distance from anode when anode current density is 50 mA/cm^2 and the distance between anode and cathode is fixed to be 310 mm.

the surface of anode where electropolishing taking place. Unlike an expected nonlinear behavior, a linear dependence was observed. Although we have performed these measurements several times, at present we do not have an explanation for the apparent discrepancy between these measurements shown in Figs. 7 and 9. Tentatively, we try to understand this result in the following way: Since the distance between anode and cathode is very long here, the applied voltage and current density are not sufficiently large to trigger chemical reaction in the electrolyte. Therefore, the whole electrolyte behaves like a resistor. It is believed that a nonlinear behavior may be observed when either the distance between anode and cathode becomes shorter or the applied voltage and current density are increased. Further investigation along this line is underway.

3.4 Comparison with KEK's results

For comparison purpose, we also did electropolishing on Nb using the KEK recipe [1]. The optimum conditions [1] were adopted and polishing lasted for half an hour. A typical optical image of a surface after polishing is shown in Fig.10a. Fig.10b shows a typical surface image of a sample electropolished for half an hour using the present recipe under the optimum polishing conditions which are defined as the turning point from the polishing area to the gas evolution area in Fig.2. The surface of Fig.10a appears to be shinier than that of Fig.10b. Some grain boundaries are still visible in Fig.10a, whereas in Fig.10b we can hardly see any grain boundaries. This fact is also well reflected from scanning electron microscope

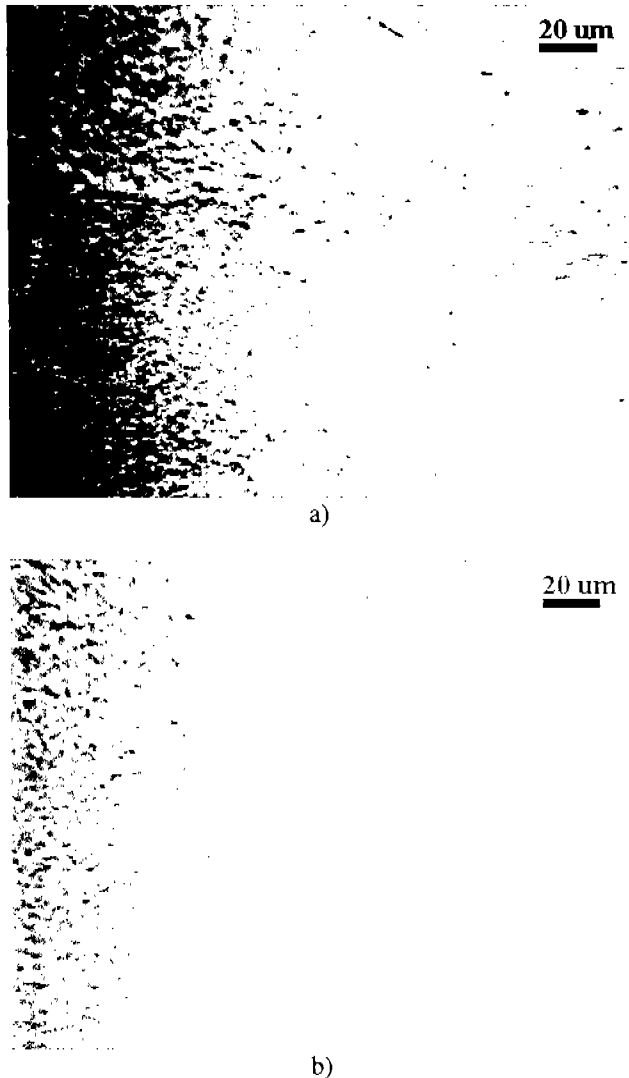


Fig.10: Typical optical images of Nb surfaces treated by the optimum electropolishing conditions for 30 minutes using the electrolyte of a) KEK's recipe and b) the present recipe. A surface pattern can be seen in image b).

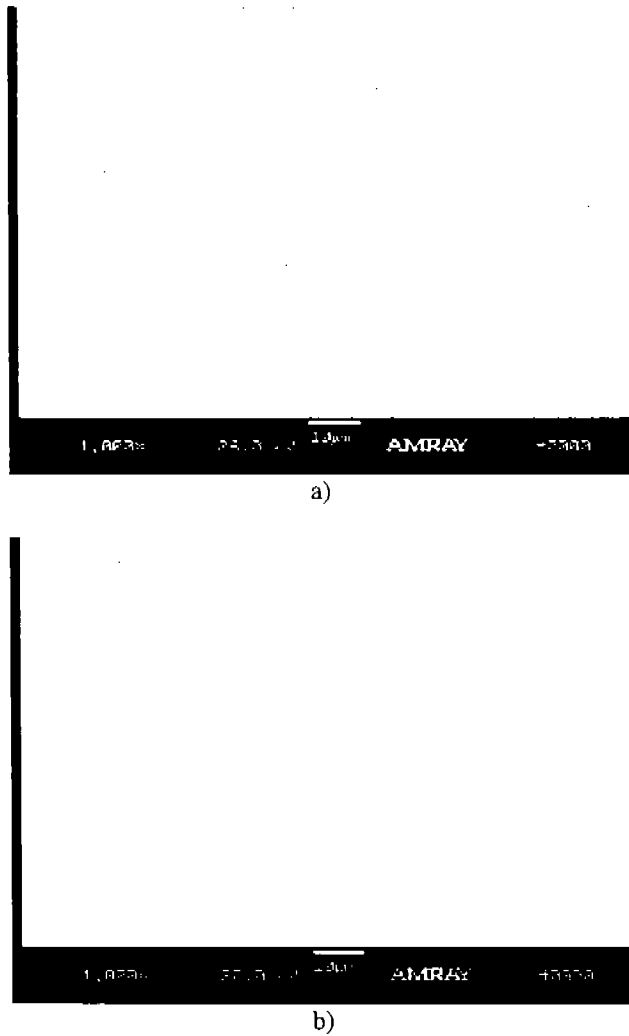


Fig.11: Typical scanning electron microscope images of Nb surfaces treated by the optimum electropolishing conditions for 30 minutes using the electrolyte of a) KEK's recipe and b) the present recipe.

(SEM) images as shown in Fig.11. Therefore, Nb surfaces polished using the present recipe tend to be smoother than those polished by KEK's recipe as judging from microscopic images. It is interesting to note that sometimes Nb surfaces polished by the present recipe under the optimum conditions have a special surface pattern similar to shallow fingerprint. This pattern can be better seen under a larger magnification using SEM as shown in Fig.12.

For Nb SRF cavities, smoothness may be more important than shininess. The shinier surface finish in Fig.10a is mainly due to the extra amount of sulfuric acid in KEK's recipe in comparison with the present recipe, since sulfuric acid is often used as brightening agent. On the other hand, it is also well known that sulfuric acid is highly hygroscopic when concentrated, and can reduce Nb removal rate when the concentration of it is increased

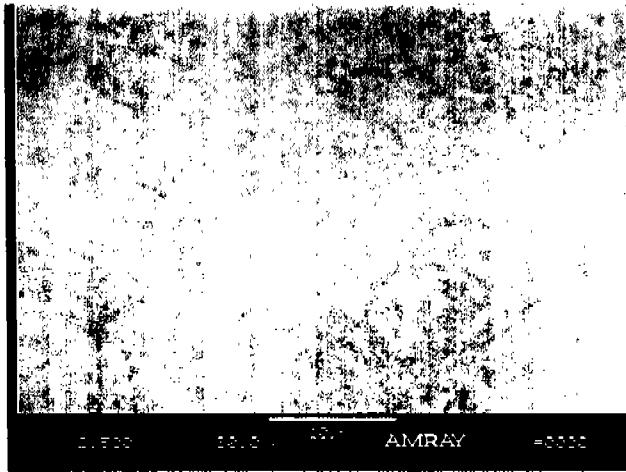


Fig.12: The surface pattern shown in Fig.10b) can also be seen by scanning electron microscope under a large magnification.

[5]. It was also found that sulfur is likely to accumulate inside the oxide layer of Nb SRF cavities [5,8], due to the presence of sulfuric acid in the electrolyte. Therefore, partial replacement of sulfuric acid by lactic acid has beneficial effects to the performance of a Nb cavity. We believe that the smoother appearance of the surface in Figs. 10b and 11b is also attributable to the partial replacement of sulfuric acid by lactic acid. One of the roles that lactic acid plays in the present electrolyte recipe is to balance the pH value of the acid mixture similar to the role of phosphoric acid in the acid mixture for BCP, although the detailed role of lactic acid is still unclear to us at this moment. Therefore, lactic acid reduces the aggressiveness of the electrolyte for etching. Etching is an inevitable process taking place during electropolishing involving hydrofluoric and sulfuric acids, even under the optimum polishing conditions. Grain boundaries and defect locations are the preferential places for etching. With the replacement of sulfuric acid by lactic acid, it slows down the etching process at grain boundaries and defect locations while increasing the Nb removal rate as discussed in Section 3.2. Both these two effects contribute to the smoother surface finish using the present recipe. Based on these considerations, for easy referring and memorization we would like to name the present electropolishing process as "Buffered ElectroPolishing" which is abbreviated as BEP.

Basically speaking, the differences between BEP and KEK's electropolishing process can be understood by the three beneficial effects of the addition of an organic acid to the electrolyte as listed in Section 3.2. Among the three beneficial effects, the first one is not completely confirmed here since our limiting current density is almost the same as that [1] of KEK, while temperature effect is not studied. The expectation of a lower limiting current density comes from the fact that lactic acid is much more viscous than sulfuric acid. Higher viscosity has been found [9,10] to reduce the limiting current

density. We have not found a reasonable explanation for this discrepancy yet.

3.5 Cathode Material

Cathode material will surely affect surface finish of an electropolished metal. Generally speaking, a selected cathode material should be as inert as possible in terms of chemical reactivity to the electrolyte involved. In reference 3, platinum was used. We also know [1] from KEK that pure aluminum is not reactive with the mixture of sulfuric and hydrofluoric acids, although it may react with each one of them individually. Since platinum is very expensive, naturally aluminum is selected as the cathode material to start with. All results presented above were obtained using pure aluminum cathode.

Some other cathode materials we intended to try included stainless steel, gold, and platinum. Since gold and platinum are very expensive, we thought about using sputtering technique to coat gold or platinum on the surface of either pure aluminum or stainless steel. Due to various reasons, only pure aluminum, stainless steel, and gold-coated pure aluminum were tried and used as cathode.

Fig.13 shows a typical image obtained on the Nb surfaces after electropolishing for half an hour when stainless steel is used as cathode. Other polishing parameters are exactly the same as the optimum conditions used for obtaining Fig.10b. Polishing rate was found to be $0.570 \mu\text{m}/\text{min}$ that is a little less than that for pure aluminum cathode. Clearly, the surface of Fig.13 is rougher than that of Fig.10b. Grain boundaries are still visible here. On the other hand, the surface pattern shown here is finer than that of Fig.10b. Therefore, the surface of each grain may be smoother. Strangely, careful searching over the whole surface revealed that at some locations of the surface, some relatively big holes were

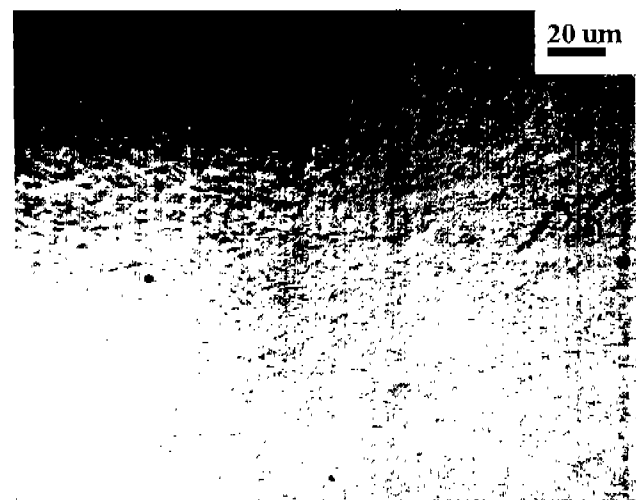


Fig.13: Typical optical image of a Nb surface treated by the optimum electropolishing conditions found for pure aluminum cathode when stainless steel is used as the cathode material. Polishing time was 30 minutes.

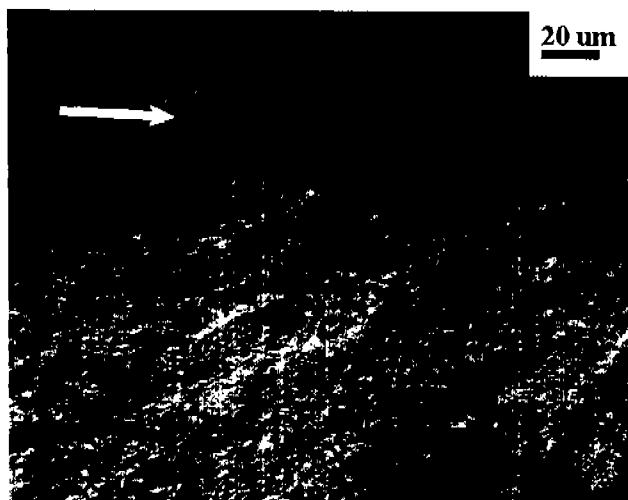


Fig.14: An example of the pits found at some locations on a Nb surface, treated with a stainless steel cathode using the optimum parameters obtained from experiments with pure aluminum cathode. Polishing time was 30 minutes.

found as shown in Fig.14. The size of these holes is comparable to those shown in Fig.5, implying therefore that they may originate from the same mechanism. If this is true, we may conclude that I_d vs. V curve for pure aluminum cathode is different from that for stainless steel cathode. Therefore for each different cathode material, a careful study of I_d vs. V curve needs to be done. Nevertheless, we can safely say that the optimum conditions for stainless steel cathode are quite close to those for pure aluminum, since most of the surface is quite flat and we could not see so many holes per certain area as that from Fig.5.

Another interesting observation is the amount of foam generated during polishing here is significantly less than that when using pure aluminum cathode. In all our BEP experiments, we found that foam was generated only on the surface of cathode when the polishing conditions adopted were not inside the gas evolution region of Fig.2. This is a very useful piece of information, since we know that hydrogen gas is normally created on the surface of cathode during electropolishing and the well-known Q disease in Nb SRF cavities is caused mainly by hydrogen. If we can manage to isolate the gases created on the surface of cathode from reaching the surface of Nb anode during BEP, in principle we can then avoid the Q disease. This would result in a significant capital saving for the cost of performing heat treatment on Nb SRF cavities. Obviously, it is easier to isolate the cathode gases by using a vertical BEP set-up than a horizontal one. Refinement and commissioning of an appropriate vertical BEP set-up for Nb cavities have been undertaken and the results will be reported in a separate paper.

When stainless steel was used as cathode, a layer of thin black material was found at some locations of the cathode surface. We tried to identify the composition of the black material using energy dispersive x-ray (EDX), but failed. The reason of failure was that the black

material was too thin to be identified by EDX. It is highly plausible that the black material is carbon or a metal oxide smut.

We also attempted to use gold-coated pure aluminum as cathode for BEP. The gold coating was, however, not adhesive to the base material enough that it was only loosely attached to the surface of the pure aluminum after half an hour BEP. We consider the results are not reliable and therefore will not be reported here. We did notice that the foam formed on the cathode surface was even less than that on the cathode surface of stainless steel. It is worth mentioning here that in reference 3, platinum was used as cathode material. Tentatively speaking, it is anticipated that better Nb surface finish may be obtained by BEP when gold or platinum is used as cathode.

3.6 Attempts to Electropolish on Nb Cavities

Polishing on Nb SRF cavities is the last and the most exciting step of this study. Here we report some

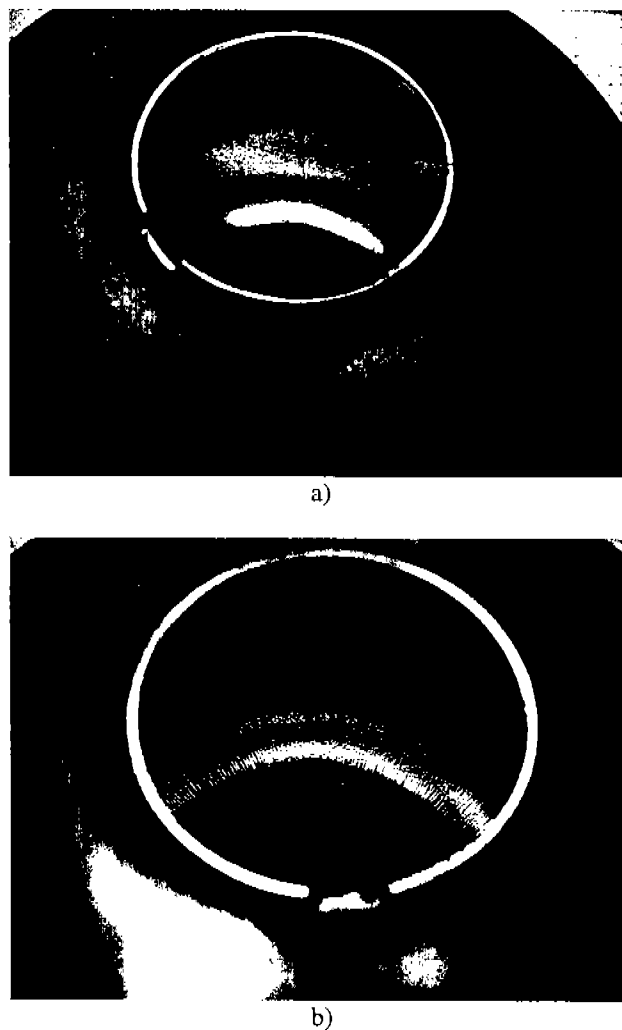
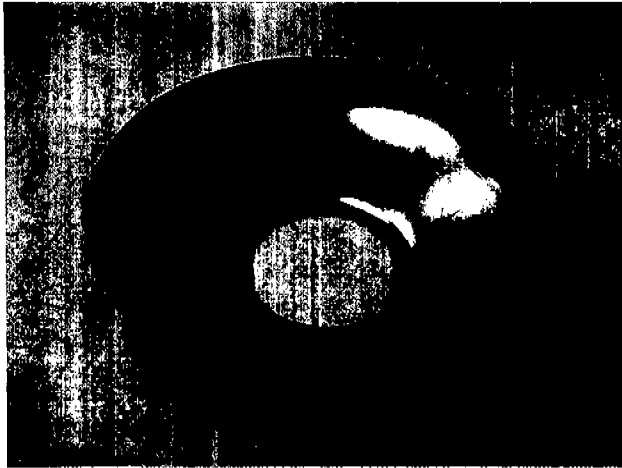


Fig.15: Pictures of a single-cell Nb cavity without any beam pipes, which was electropolished using the present electrolyte. Process time was 60 minutes and a pure aluminum rod was used as the cathode. Polishing took

place only on iris areas. a) picture shows the bottom iris area and b) picture shows the upper iris area (see text for details).



a)



b)

Fig.16: Pictures of a half-cell Nb cavity a) before electropolishing and b) after electropolishing for 30 minutes using a special shape of cathode which has a more uniform distance between cathode and anode.

preliminary results. Polishing was done by simply immersing vertically a single cell cavity without any beam pipes into the BEP electrolyte and the cathode used was a pure aluminum rod. Polishing current was calculated by multiplying the total surface area of the cavity with 50 mA/cm^2 . Fig.15 shows how the cavity looks like after one hour polishing. It seems that only the lower part of the area close to iris was polished as shown in Fig.15a. Large amount of foam was generated during BEP, which led to the trace of gas movement near the upper part of the area close to iris (Fig.15b). Almost no

electropolishing took place at equator region of the cavity, indicating the important effect of the variation of the distance between anode and cathode on the surface finish during BEP.

Better results were obtained when the distance between anode and cathode was arranged in a more uniform way by changing the shape of cathode. As shown in Fig.16, a better surface finish can then be obtained after polishing for only 30 minutes.

4 CONCLUSION

We are exploring an alternate electrolyte composition for electropolishing on Nb at JLab. Several essential parameters that determine the surface finish of electropolished Nb have been studied and the optimum conditions have been established. This polishing process is referred to as "Buffered ElectroPolishing" (BEP). Our preliminary results indicate that BEP is a very promising method for the treatment of Nb cavities. In progress are tests on single cell cavities to assess the RF properties of surfaces prepared by this process.

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