

EVALUATION OF THE DIFFUSION COEFFICIENT OF FLUORINE DURING THE ELECTROPOLISHING OF NIOBIUM^{*}

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Abstract

Future accelerators, such as the envisioned international linear collider (ILC), require unprecedented cavity performance, which is strongly influenced by interior surface nano-smoothness. Electropolishing (EP) is the technique of choice being developed for high-field SRF cavities. Previous study has shown that the mechanism Nb electropolishing proceeds by formation and dissolution of a compact salt film under fluorine diffusion-limited mass transport control. We pursue an improved understanding of the microscopic conditions required for optimum surface finishing. The viscosity of the standard electrolyte has been measured using a commercial viscometer, and the diffusion coefficient of fluorine was measured at a variety of temperatures from 0°C to 50°C using an Nb rotating disk electrode. In addition, data indicate that electrode kinetics is becoming competitive with the mass transfer current limitation and increases dramatically with temperature. These findings are expected to guide the optimization of EP process parameters for achieving controlled, reproducible and uniform nano-smooth surface finishing for SRF cavities.

INTRODUCTION

With routine operation of EP facilities in recent years, more multicell SRF cavity test data have become available. Cavity performance variability has emerged as a major challenge for electropolishing processed niobium cavities [1], especially for the ILC, the most visible to the public, with 16,000 9-cell cavities intended to perform at historically high acceleration gradient (>31 MV/m). One outstanding variability issue is the unpredictable onset of field emission. Another is the quench field, which has been observed to vary unpredictably in electropolished cavities in the absence of field emission. Ongoing progress against field emission relies on elimination of surface adhering particles by improved cleanliness and high pressure rinsing. Quenches without x-ray emission are usually associated with defects: foreign material inclusions, weld beads, etch pits and mechanical damages are severe examples. At present, besides reducing the incidence of severe defect-induced quenches via improved quality control of manufacturing practice, a complete understanding of process parameters and adequate process control are very important to help achieve reproducible high gradient cavities.

Electropolishing is a surface finishing process based on anodic dissolution of a metal or alloy in an appropriately chosen electrolyte [2]. It is characterized by the elimination of micro-roughness (leveling) and the absence of crystallographic and grain boundary attack (brightening) and results in the production of smooth, bright surfaces [3-4]. Leveling results from the fact that protruding parts of a rough surface dissolve faster than recessed parts. This can be achieved under either ohmic or mass transport control [4]. Brightening can only occur under mass transport control, which suppresses crystallographic etching [4-6]. The supply and removal of reactant and product contribute to three different forms of mass transport (i) diffusion, defined as the movement of species due to concentration gradient; (ii) convection, in which the movement is due to external mechanical energy—for example, electrode rotation; (iii) migration due to a potential gradient—that is, only charged species are affected [7].

In the previous study, electrochemical impedance spectroscopy and related techniques point to the electropolishing mechanism of Nb in a sulphuric and hydrofluoric acid electrolyte as controlled by a compact surface salt film under fluorine diffusion-limited mass transport control [8]. A detailed understanding about the diffusion of fluorine is still missing. In the present work, we report determination of the diffusion coefficient of fluoride ion in EP solution using a Nb rotating disk electrode at different temperatures. A rotating disk electrode (RDE) is a device that creates a totally defined solution flow pattern in which the mass transport of limiting species is almost completely due to convection [7,9]. This property allows the RDE to be used to calculate parameters related to mass transport, such as the diffusion coefficient of various electroactive species.

EXPERIMENTAL STUDIES

For RDE experiments, a high purity polycrystalline Nb disc electrode sample was inserted in a Teflon holder with a reactive surface area of 0.19 cm². The Nb discs were mechanically polished up to 4000 grit emery paper, ultrasonically rinsed with distilled water and isopropanol and air dried. A high purity Al wire was used as the counter electrode. The Gamry RDE710 rotating disc electrode setup was used for the experiments. The reference electrode was a saturated mercury/mercurous sulphate electrode (MSE). The electrolytes were prepared from 49% hydrofluoric and 96% sulphuric acid.

The polarization curves were measured stepwise (step size=0.1 volts, dwell time=0.25 second) over the potential range from 0 to 22 volts. The potential between the Nb electrode and the reference electrode was recorded using

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a Keithley 6517A electrometer. The addition of the reference electrode allows monitoring of the potentials on the cathode and anode independently. The current was recorded with a Keithley 2000 multimeter. Prior to the polarization measurements, the electrodes were immersed in the electrolyte in an open circuit condition for 3 to 5 minutes.

The electrolyte viscosities were measured with a Brookfield DV-II+PRO digital viscometer at different temperatures, and the electrolyte density was measured by weighing the electrolyte in a Teflon volumetric flask. The variation of repeated viscosity measurements was about 1.5%. The reported diffusion coefficients were verified by repeated experiments, with typical variations in limiting current densities of about 2%.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Anodic Polarization Curves under RDE

The anodic polarization curves were determined for 1:10 volume ratio of HF and H₂SO₄ electrolyte at the different angular velocities of the Nb disk electrode at several temperatures (1°C, 9°C, 19°C, 30°C, 41°C and 50°C). Figure 1 shows a typical anodic I-V curve for Nb electropolishing on the rotating disk at 9°C, and similar curves have been obtained at the other temperatures studied here. All the curves exhibit a well defined and a wide potential range of limiting current density plateau. It suggests the existence of a salt film, possibly Nb₂O₅ [8,10], and the dissolution rate is mass transport controlled and involves diffusion of limited species through a Nernst diffusion layer [8,10]. Figure 2 shows the typical dependence of the limiting current density on the square root of rotation rate [11]. The limiting current density values were determined on the current plateau at a potential of 6V. The variation of the limiting current density shows a linear behaviour with distinct slope, which provides further evidence that the supply of reactant, such as F ion or its related species (HF⁻ or HF [10]), is under mass transport control. However, the non-zero offsets at the higher electrolyte temperatures indicate the presence of an electrode kinetic mechanism; we assume it to be chemical etching that proceeds in parallel with the diffusion limited mass transport and increases dramatically with the electrolyte temperature.

Diffusion Coefficient of Fluorine

By solving the convective diffusion equation with the boundary conditions of the hydrodynamic velocity profile, the Levich equation (Eq. 1) can be used to describe the relationship of limiting current density j_L , to the physical properties of the electrolyte bath [7, 10-14],

$$j_L = 0.62nFD^{0.67}v^{-0.166}c\omega^{0.5} \quad (1)$$

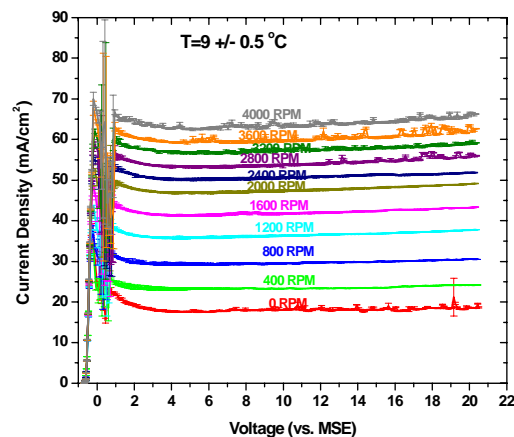


Figure 1: The anode polarization curves of Nb in 1:10 volume ratio HF and H₂SO₄ at 9 °C.

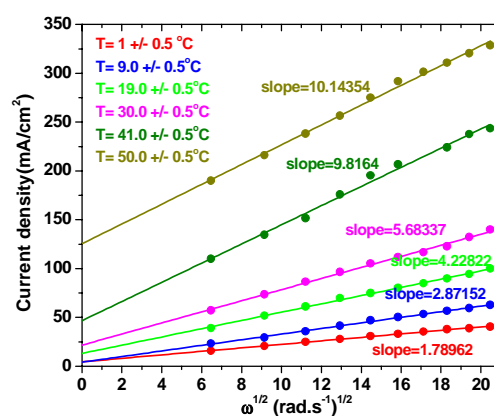


Figure 2: The limiting current density plotted as a function of the square root of rotation rate at a potential 6V (vs. MSE).

Here, n is the number of electrons involved in electrode reaction, for fluorine n equals 1, F is the Faraday constant, 96470 C.mol⁻¹, v is the kinematic viscosity in m².s⁻¹, c is the concentration of electroactive species in bulk solution in mol.m⁻³ (the concentration of fluorine in 1:10 HF/H₂SO₄ studied here is 2670 mol.m⁻³), and ω is the rotation speed in rad.s⁻¹. Note that

$$\text{slope}(j_L \text{ vs. } \omega^{0.5}) = 0.62nFD^{0.67}v^{-0.166}c. \quad (2)$$

Hence, a test for pure mass transport control is that the plot of j_L vs. $\omega^{0.5}$ is linear and passes through the origin [10]. The corresponding diffusion coefficient D (m².s⁻¹) can then be determined when the kinematic viscosity of electrolyte is known. Table 1 lists the measured dynamic viscosity, and calculated diffusion coefficient of fluorine in the EP solution under different temperatures.

Temperature (°C)	Dynamic Viscosity (cP)	Diffusion Coefficient (cm ² /sec)
1	40.7	2.69 E-08
9	34.2	4.44 E-08
19	26.3	8.77 E-08
30	20.8	1.29 E-07
41	18.1	2.83 E-07
50	16.5	2.90 E-07

Table 1: The measured dynamic viscosity of 1:10 HF/H₂SO₄ electrolyte and calculated diffusion coefficient of fluorine at 1°C, 9°C, 19°C, 30°C, 41°C and 50°C.

The Diffusion Limited Mass Transfer Produces the Nano-smooth Surface Finishing

According to the Nernst diffusion layer model, the electrolyte can be divided into two zones. The first region closest to the surface of the electrode with the thickness δ , which is named the Nernst diffusion layer, where it is assumed that there is totally stagnant layer and thereby diffusion is the only mode of mass transport. The limiting current density is given by equation 3.

$$j_L = nFDc/\delta \quad (3)$$

So, for a given diffusion limited current density, fluorine concentration, and measured diffusion constant, one can calculate the effective thickness of the diffusion layer. In the second region outside the Nernst diffusion layer a strong convection occurs and all species concentrations are considered as constant.

In this study, the Nernst diffusion layer thickness was experimentally determined. It is 8~20 μm over the temperature range 10°C~30°C for the standard 1:10 volume ratio of HF/H₂SO₄ electrolyte. It is the concentration gradient within this layer that is expected to produce the desired polishing. The Figure 3a and 3b are two Nb samples centrifugal barrel polished by KEK [15]. We label them as rough CBP and fine CBP according to the different sizes of polishing media and the different durations used. The details of treatment can be found in reference [16]. The AFM results in 50 μm ×50 μm scanning area show that the rough CBP treated sample has the 889.6±32.5nm average surface mean square root roughness (R_q), and the average surface variation (R_z) is above 5.3 μm . Respectively, R_q is 178±32.5nm and R_z is about 1.6 μm for fine CBP. After 100 minutes of EP polishing (30 μm removal) by 1:10 volume ratio HF/H₂SO₄ at 30±1°C, the fine CBP surface achieves a best finishing, with 54.9±4.5nm mean square root roughness (see Figure 3d), and the surface variation is about 150nm, as compared with the rough CBP, where R_q is 187.5±22.1nm and R_z is about 1.6 μm (Figure 3c). This results gives strong evidence that diffusion limited mass transfer would produce the nano-smooth surface finishing. Further refinement of the polishing analysis as a function of temperature is planned in the near future.

09 Cavity preparation and production

CONCLUSION

In this investigation, the Nb electropolishing was studied using a rotating disc electrode in a 1:10 volume ratio of HF/H₂SO₄ electrolyte at different temperatures. The limiting current density demonstrates a clear dependence on fluorine diffusive mass transport. However, a parallel electrode kinetics process has been identified, which is independent of mass flow condition and polarization potential, but strongly depends on temperature. This suggests that high temperature may activate an etching process that recognizes different grain orientations, resulting in a non-uniform surface finishing instead of brightening. The viscosity of the standard HF/H₂SO₄ electrolyte strongly depends on the electrolyte temperature. The analysis yields effective diffusion coefficient for fluoride ion on the order of 10⁻⁸ ~10⁻⁷ cm².s⁻¹ under the temperatures studied. This study is expected to improve the fundamental understanding needed to guide the optimization of EP of niobium for SRF cavities.

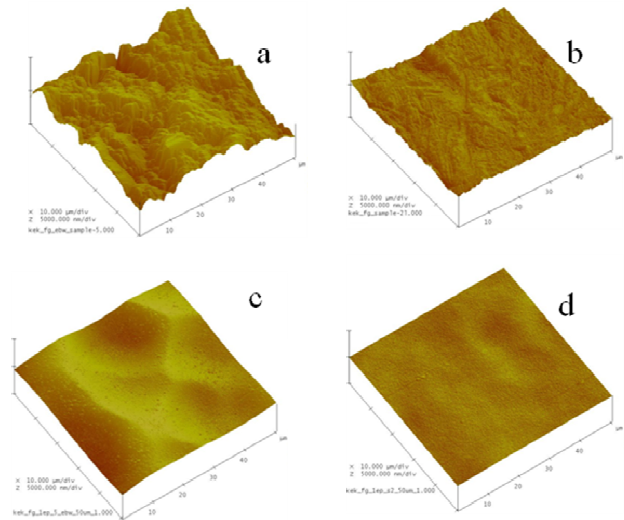


Figure 3: AFM images of CBP polycrystalline Nb samples before and after 100 minutes electropolishing at 30±1°C (a) rough CBP (b) fine CBP (c) rough CBP after electropolishing (d) rough CBP after electropolishing.

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