Field emission from crystalline niobium

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Appreciable suppression of field emission (FE) from metallic surfaces has been achieved by the use of improved surface cleaning techniques. In order to understand the effects of surface preparation on field emission, systematic measurements were performed on five single crystal and three large grain samples of high purity (RRR > 300) niobium by means of atomic force microscope, x-ray diffraction, scanning electron microscope (SEM), and dc field emission scanning microscope. The samples were treated with buffered chemical polishing (BCP), half of those for 30 μm and others for 100 μm removal of surface layer, followed by a final high pressure water rinsing. These samples provided the emission at minimum surface fields of 150 MV/m and those with longer BCP treatment showed the onset of field emission at slightly higher fields. A low temperature (~150°C) heat treatment in a high vacuum (10^-6 mbar) chamber for 14 hours, on a selected large grain Nb sample, gives the evidence for the grain boundary assisted FE at very high fields of 250 and 300 MV/m. Intrinsic field emission measurements on the present Nb surfaces revealed anisotropic values of work function for different orientations. Finally, an interesting correlation between sizes of all investigated emitters derived from SEM images with respect to their respective onset fields has been found, which might facilitate the quality control of superconducting radio-frequency cavities for linear accelerators.

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I. INTRODUCTION

Highly purified fine grain niobium sheets (RRR > 250) have been used worldwide for the fabrication of high gradient superconducting accelerator cavities in various projects like FLASH [1], SNS [2], and RIA [3]. Much attention has been given to the surface preparation and cleanliness techniques, which has suppressed significantly the enhanced field emission (FE) of electrons from the cavity surface and thus improved the regular cavity performance at high accelerating gradients, e.g., up to about $E_{\text{acc}} = 30 \text{ MV/m}$ for nine-cell 1.3 GHz structures [4].

High pressure rinsing (HPR) with ultrapure water is used as a standard technique for the final cleaning of such cavities [5], while dry ice cleaning (DIC) has emerged recently to be a very effective tool in this respect [6]. The best DIC single crystal Nb sample did not provide any FE up to an electric surface field $E_s (=2E_{\text{acc}})$ of 250 MV/m. Further, the removal of field emitting particulates down to 400 nm size and partial smoothing of protrusion edges by DIC on the Nb surface was also reported. On the other hand, for the HPR method it is known that the typical pressures of 80–100 bar theoretically overcome the sticking force for particles of about 1–2 μm size [5].

An approach towards improving the cavity fabrication for future linear accelerators like XFEL [7] and ILC [8] has been made by using buffered chemically polished (BCP) large grain Nb (LGNb) or single crystal Nb (SCNb) instead of electropolished (EP) polycrystalline Nb, which might be less expensive due to the elimination of sheet fabrication and related processes. Preliminary tests of single-cell cavities made from large grain Nb have yielded $E_{\text{acc}}$ up to 45 MV/m, which is one of the highest values achieved yet [9]. Further research on multicell structures made from large grain or single crystal Nb is required before it can replace polycrystalline Nb. It has also been reported recently that the grain boundaries on large grain Nb cavities provide some, although not dominant, contribution to the hot spots in corresponding thermal maps [10]. Since grain boundaries get easily contaminated by the segregation of impurities during the usual bakeout of cavities [11,12], it is interesting to investigate their role for field emission, too [13].

In this paper, we report on FE properties and surface characteristics of eight large grain and single crystal samples, measured by means of field emission scanning microscope (FESM) [14–16], scanning electron microscope (SEM), atomic force microscope (AFM), and x-ray diffraction (XRD). In situ heat treatments at 150°C were performed on two samples and then measured again to find any change in corresponding FE properties. Intrinsic FE measurements on such high quality samples were possible due to their very smooth surfaces and the derived $\phi$ values for different crystal orientations will also be discussed here. Finally, a correlation between sizes of all investigated emitters derived from SEM images and their respective onset fields will be presented.
II. SAMPLE PREPARATION AND SURFACE QUALITY CONTROL

Five single crystal and three large grain Nb samples of 28 mm diameter were fabricated at DESY Hamburg. The RRR value of the material was at least 300 with Ta content of ∼300 ppm. First of all, the sample disks were produced by high pressure water jet cut of 30 mm diameter ingots followed by mechanical polishing of the surface up to $R_d < 0.1 \mu m$. These were then oxypolished and etched up to ∼5 μm, and annealed at 800°C for 2 hours to relieve the mechanical stress in the material. Afterwards the disks were electron beam welded to specially designed sample holders. Final surface preparation using BCP in HF(40%):HNO$_3$(65%):H$_3$PO$_4$(85%) in volume ratio 1:1:2 at temperature 12–18°C has resulted in a mirrorlike surface. For half of the samples a surface damage layer of 30 and 100 μm was removed, respectively, with the intention of finding the impact of longer BCP treatment on the FE properties of the sample surface. The details of samples with surface preparation, crystal orientations, and roughness are summarized in Table I.

The high resolution optical microscopic images of samples SCNb5 and LGNb3 in Figs. 1(a) and 1(b) demonstrate the appearance of different grains of niobium, and the AFM image in Fig. 1(c) provides the surface roughness value of 7.5 nm for Nb(100) oriented surface [Fig. 1(d)]. 100 μm polished single crystal Nb surfaces possess less surface roughness (6–7.2 nm) than 30 μm polished ones (12–17.5 nm), while the large grain samples become as smooth only for 100 μm BCP. All the samples were especially marked during fabrication to adjust the sample po-

| Sample | Removed material using BCP | Orientation | Surface roughness |
|--------|---------------------------|------------|------------------|
| SCNb1  | 30 μm                     | (110)      | 11.7 nm          |
| SCNb2  | 30 μm                     | (110)      | 17.6 nm          |
| SCNb3  | 100 μm                    | (110)      | 7.0 nm           |
| SCNb4  | 100 μm                    | (111)      | 6.2 nm           |
| SCNb5  | 100 μm                    | (100)      | 7.5 nm           |
| LGNb1  | 30 μm, 100 μm, 110 μm     | (110), (111), (110) | 100, 110.5, 62.7 |
| LGNb2  | 30 μm                     | nm         | nm               |
| LGNb3  | 100 μm                    | (100), (110), (111) | 8.8, 6.9, 6.8   |

FIG. 1. (Color) (a) High resolution optical microscope image of sample SCNb5, (b) microscopic view of intersection of grain boundaries on large grain sample LGNb3, (c) AFM image of sample SCNb5 showing root mean square roughness of 7.5 nm over (80 × 80) μm$^2$ area, and (d) XRD image of SCNb5 revealing (100) orientation.
position in different experimental setups and were finally rinsed with ultrapure water using a high pressure of 150 bar (nominal value for the used HPR system).

The FE measurements were performed on the flat Nb cathodes under ultrahigh vacuum conditions in FESM, using conical anodes. The samples were first scanned over a selected area of (12 × 12) and (10 × 10) mm² at 90 and 120 MV/m with 300 μm anode, and then at 150 and 200 (or 250 and higher) MV/m with 100 μm anode over the areas of (7.5 × 7.5) and (5 × 5) mm², respectively. During scans, the applied voltage was regulated for 2 nA current and anode-to-sample distance was varied from 50 to 20 μm according to the required field using 5 kV power supply. The strong emitters in the observed electric field (E) maps were localized and studied for their individual FE properties. A resistive heating oven installed in the high vacuum chamber of FESM was used to heat the samples at 150(±10)°C. Efforts were made finally to identify the emitters ex situ in SEM and to reveal their origin from geometrical features and chemical compositions with energy dispersive x-ray analysis (EDX).

III. FIELD EMISSION RESULTS AND DISCUSSION

A. Statistical overview of the emitters

All large grain and single crystal Nb samples have provided very good results, as summarized in Table II. FE maps on large grain Nb samples showed the onset of FE for 2 nA current at 120 MV/m for 30 μm and at 150 MV/m for 100 μm polished surfaces. For single crystal Nb samples with 30 and 100 μm BCP, the onset of FE was observed at 150 MV/m and 200 MV/m, respectively. The typical FE maps, given in Fig. 2, show the observed emitters at the highest scanned field levels for these two cases. If we compare the number of emitters at different field levels for all samples from Table II, a marked difference between 30 μm BCP’d LGNb samples (LGNb1 and 2) and all others is observed. It is interesting to discover that it can be directly related to the large difference in the surface roughness values, which is of the order of 100 nm for former and about 10 nm for the later (Table I). Thus, FE was strongly suppressed for smoother surfaces.

A statistical overview of the number density of emitters N for varying electric field E is presented in Fig. 3. In order to reduce the statistical error and to simplify the N(E) plot, all the results for a particular kind of sample have been summed up, i.e., the corresponding areas and number of emitters were added at the given scanned field levels. Within statistical errors, for LGNb with 30 and 100 μm BCP, the onset of FE was observed at 120 and 150 MV/m, while for SCNb at 150 and 200 MV/m, respectively. Despite a significant statistical error, for more material removal there is a tendency of N(E) exponential fit lines to shift to the right, i.e., to higher onset fields and an evidence for reduced slopes, i.e., less number density of field emitters at a given field level. For comparison with the best quality polycrystalline Nb sample¹ electropolished inside a cavity at DESY [17,18], the corresponding fit line has also been plotted, showing clearly the better performance of SCNb and LGNb samples. These observations are consistent with the earlier findings that more than 50 μm of the material thickness has to be removed for better cavity performance [19,20].

As it is noticeable above that these samples could be measured at very high fields (150–200 MV/m), this is not the case for rf cavities. The tests on large grain Nb rf cavities (six single-cell and three nine-cell) performed until now at DESY showed that the maximum gradients typically achieved are around 40 MV/m (i.e. 80 MV/m surface fields). In most of the cases, it was not limited by FE but by local thermal breakdown (quench) [21]. The BCP treated (80–100 μm) large grain Nb cavities reached up to

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¹The polycrystalline Nb sample, made up of cavity material, was EP'd up to 144.8 μm in the first step using H₂SO₄ (95%) and HF (46%) in a volume ratio of 9:1, and was mounted inside a cavity during final 43 μm EP and HPR. The sample surface showed the microroughness of ~0.2 μm and grain boundaries of 1–2 μm step height. The cavity reached 26.5 MV/m without x rays being detected.
While a single-cell cavity of single crystal Nb showed field up to 38 MV/m [22], though a systematic study is required for better understanding on the effect of surface preparation on cavity performance, for this purpose eight new large grain Nb nine-cell cavities have been fabricated and will be tested at DESY after BCP treatment only.

**B. Grain boundary effects and low temperature heat treatment**

Present high quality Nb samples should be informative to study any grain boundary effect on FE, due to the presence of either no grain boundary or very few but large grain boundaries easily visible on the sample surface. However, no FE was observed from grain boundaries up to the field of 250 MV/m from any of the as-prepared large grain Nb samples.

Heat treatment (HT) of polycrystalline Nb cavities at low temperatures (100–150°C) is used as a final preparation step, which improves the quality factor of cavities probably by the diffusion of oxygen from surface oxide into the bulk niobium [23,24]. Analogous to this cavity treatment, we have selected two samples LGNb3 and SCNb4 for low temperature heat treatments at 150°C for 14 and 8 hours, respectively. The corresponding FE maps made after HT are shown in Fig. 4. It is interesting to find that, on the LGNb sample, most of the emitting sites were activated near or on the grain boundaries, which are 89% at 250 MV/m and 63% at 300 MV/m of the total number of emitters. No features in SEM were observed corresponding to these emitters. Two grain boundaries possessing more emitters nearby have the step height of ~12–15 μm, while the third one has the step height less than 0.5 μm, as measured by the profilometer [Fig. 4(a)]. Further it is notable that the strongest emission is observed at the intersection of three grain boundaries. On the other hand, the number of emitters for SCNb remained unchanged up to 200 MV/m as before HT, while at 250 MV/m, one new emitter appeared, and three old emitters disappeared [Fig. 4(b)]. Within statistical error, low temperature HT on SCNb did not show any change on its FE properties. Thus, the first evidence for grain boundary assisted FE is observed on LGNb, but only after HT. This is due to easier segregation of impurities along grain boundaries during HT. Our results also show the need for performing similar measurements at higher temperatures for comparison with 800°C annealing of cavities. More samples measurements are required for a better understanding of grain boundary effects on FE, and should be analyzed with SEM before and after HT.
C. Single emitter investigations

The strong emitters appearing in the FE maps of all scanned samples were localized in FESM as well as in SEM (later on) to study their individual FE characteristics with respect to their physical properties. In all cases, the observed emission confirmed Fowler-Nordheim (FN) theory [25] with local field enhancement [26–28]. Moreover, the phenomena of activation, deactivation, and stabilization of the emitters were generally observed in the continuous up and down cycles of applied electric fields during I-V measurements. The typically observed values of field enhancement factor $\beta$ and emission area $S$ for different samples are given in Table II, where $\beta$ ranges from 24 to 56 and $S$ varies from $10^{-4}$ to $10^{-8}$ $\mu m^2$. Compared to this the $\beta$ typically observed in cavities are higher, lying in the range 60–120, which was observed for both the large grain as well as fine grain Nb cavities at surface fields of 40–80 MV/m.

The features observed for emitters in SEM investigations were generally surface irregularities (67%) and particulates (33%) with or without foreign elements present. On 100 $\mu m$ polished samples, the presence of a foreign element (aluminum) was detected only in one case [Fig. 5(a)], which might have come from the Al caps used in the transport system of the samples. The corresponding FN curves are changing in different increasing and decreasing modes of electric fields showing the emitters not being stable and might not be properly connected to the surface. The retrieved $\beta$ value of 26 and $S$ value of $6 \times 10^{-6} \mu m^2$ seem reasonable for the nm size sharp features present on this flakelike object, which might dominate to the local field enhancement.

In the case of heat treated samples, it was interesting to find that the FN curves of all the emitters were rather straight, i.e., showing stable FN behavior probably due to good contact of emitters with the smooth surface. A typical

FIG. 4. (Color) (a) $E$ maps of LGNb3, and surface profile showing grain boundaries. The encircled emitter is the one activated before HT, and dotted lines in the scan represent the grain boundaries. (b) $E$ maps for SCNb4: the vertical shift of scans before and after HT is an experimental artifact. All the scans were made over the same area of $5 \times 5$ mm$^2$, scanned before (upper) and after 150°C heat treatment (lower row) up to the given maximum fields. An anode of 100 $\mu m$ flat-apex diameter at the tip-to-sample distance of 20(16.5) $\mu m$ for 250(300) MV/m maximum field was used in these measurements.
example is given in Fig. 5(b). The retrieved $\beta$ and $S$ values on HT samples were found in the range of $(12–57)$ and $(10^{-3}–10^{-7}) \text{ m}^2$, respectively, which are very reasonable for a nanometer to subnanometer size effective emission area.

D. Intrinsic FE measurements

The superior quality of presented single crystal Nb samples makes them suitable for intrinsic FE measurements. These measurements require absolutely clean cathode surface and anode tips, and a very small vacuum gap (down to 2 $\mu$m) for gaining high fields of $\sim 1$ GV/m by means of the 5 kV power supply. Samples SCNb4 of (111) and SCNb7 of (100) orientation were measured in defect-free areas with the freshly prepared W anodes of 5–20 $\mu$m tip diameter. Since the measurements were very much sensitive to system vibrations, the anode tips as well as the sample surface were often damaged during measurements by microdischarges [inset of Fig. 6(a)]. The measured FN curves exhibit real FN-like behavior (Fig. 6), showing the onset of FE at fields higher than 1 GV/m. Assuming $\beta$ equal to one for our smooth and single crystal samples, we retrieved the $\phi$ values of Nb with respect to different orientations from FN curves. The fitted mean $\phi$ values for Nb (111) and Nb (100) are 4.05 and 3.76 within the error of 17% and 27%, respectively. It should be noted here that, despite the usual presence of surface oxides of about 30–60 Å on niobium [29], the retrieved $\phi$ values are in accordance to literature data for the given orientations of Nb [30,31]. Earlier reported intrinsic measurements on chemically polished polycrystalline Nb have resulted in $\phi$ values of about 2 on considering a work function $\phi$ of 4 eV for Nb [32]. On the basis of these results, we conclude that, according to the effective protrusion model [33], surface roughness surely enhances the $\beta$ of particulates and thus the field emission of polycrystalline Nb cavities.

E. Emitter size vs onset electric field ($E_{on}$)

In the past three years, we have measured many samples with different types of Nb surfaces (EP polycrystalline and BCP large grain or single crystal). The analysis of localized
emitters in FESM and SEM has resulted in a suggestive plot (Fig. 7) of emitter size derived from SEM images vs corresponding onset electric fields. Particulate emitters are represented there with their average size and surface irregularities with their widths, because, e.g., for a scratch it is the parameter deciding over the height of the edges which causes enhanced FE. A huge spread in the emitter size is observed in the plot. The diagonal line, however, is referred as a threshold for the minimum emitter size and correspondingly achievable onset fields. Accordingly, to achieve an accelerating gradient of $30(40) \text{MV/m}$ for XFEL [7] (ILC [8]), surface defects larger than $3(1.3) \mu \text{m}$ must be avoided. This result will surely be useful for the quality control of superconducting structures during the assembly of large accelerator projects.

IV. CONCLUSIONS

Single crystal and large grain Nb samples treated with BCP/HPR as a final surface preparation step have been found to show no FE up to surface electric fields of $150 \text{MV/m}$. The onset fields were slightly higher for the samples with a $100 \mu \text{m}$ removed damage layer than those with $30 \mu \text{m}$, and also for single crystals compared to large grain samples due to reduced surface roughness. Heat treatment of large grain Nb sample at $150^\circ \text{C}$ for 14 hours has given first evidence for grain boundary assisted field emission. Intrinsic FE measurements revealed anisotropic $\Phi$ values of 4.02 and 3.8 for (111) and (100) orientations of Nb, respectively. From the past three years enhanced FE investigations on different Nb surfaces, a correlation between size of emitters and onset fields is obtained, which sets a threshold for the tolerable defect size to achieve the envisaged accelerating gradients in superconducting cavities reliably.

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