INFLUENCE OF HEAT TREATMENTS ON FIELD EMITTERS ON Nb CRYSTALS
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Abstract
Systematic investigations of the influence of heat treatments on parasitic field emitters (1 nA) up to activation fields of 160 MV/m on high-purity Nb samples at temperatures between 122°C (24 h) and 400°C (2 h) are reported. Two large grain and two single crystal Nb samples with typical preparations (40 μm BCP, 140 μm EP and final HPR at DESY) were used. For all samples a significant increase of the emitter number density with increasing T up to 32 emitters/cm² at 400°C were obtained, the strongest of which emitted already at 40 MV/m. The dependency of the emitter number density on the insulating Nb₂O₅ layer thickness is discussed.

INTRODUCTION
Enhanced field emission (EFE) from particulate contaminations and surface irregularities is one of the main field limitations of the superconducting Nb cavities required for the ILC. Systematic investigations on large grain (LG) and single crystal (SC) Nb have revealed an exponential increase of the emitter number density N with activation field \(E_{\text{act}}\) and EFE at much lower onset fields \(E_{\text{on}}\) (1 nA) of activated emitters. This emitter activation can be caused either by high \(E_{\text{act}}\) partially combined with microdischarges or by heat treatments (HT) at temperatures T between 120 and 800°C [1]. In cavities EFE activation by high T may also arise due to enhanced RF losses of particulates which are thermally isolated from the cavity surface. Moreover, HT between 120 and 800°C are integrated in the usual cavity fabrication process [2].

Previous EFE measurements on polycrystalline [3,4] as well as LG and SC [5] Nb samples have shown, that a strong emitter activation occurs after HTs at 400°C with low \(E_{\text{on}}\) ≥ 40 MV/m, and remaining particulates and surface defects were identified as emitters. Since the EFE activation is rather weak at 120°C, a decrease of the natural insulating Nb₂O₅ layer thickness due to HT has been suggested as main reason for their EFE activation [1]. Therefore, we have started more detailed systematic EFE measurements on LG and SC Nb samples before and after different HT between 120 and 400°C.

EXPERIMENTAL DETAILS
Measurement Techniques
For the systematic EFE measurements we have used a non-commercial ultra-high vacuum (p ~ 10⁻⁹ mbar) field emission scanning microscope (FESM) as shown in Fig. 1 [6]. Flat samples up to 25×25 mm² can be investigated after surface tilt correction relative to the truncated cone anode (\(\Theta = 300 \mu \text{m}\)) in order to achieve a constant gap \(\Delta z\) within ±1 μm for a typical (±5 mm) scan area. The FESM employs a PID-regulated power supply FUG HCN100M-10000 (10 kV, 10 mA) controlled by the EFE current as measured with an analog electrometer Keithley 610C or a digital picoammeter Keithley 6485. Non-destructive voltage scans \(V(x,y)\) for a limited EFE current \(I = 1 \text{nA}\) were performed with a resolution of 150 μm to localize emitters and to determine their N as function of \(E_{\text{act}}\) in reasonable steps (1 kV). Using the average \(\Delta z = 50 \mu \text{m}\) estimated from the long range optical microscope image, electric field maps \(E(x,y)\) up to 160 MV/m were derived.

For most emitters of each map, I(V) characteristics were locally measured up to 1 nA. The actual local field \(E_{\text{on}}\) was calibrated for each emitter as slope of a PID-regulated \(V(z)\) plot for 1 nA. Using the modified Fowler-Nordheim law [8]

\[
I_{\text{FN}} = A e^2 \frac{S_{\text{FN}} \beta_{\text{FN}} E^2}{\varphi t^2 (y) \exp \left( -B \frac{\varphi^3}{\beta_{\text{FN}}^2} v(y) \right)}
\]

the field enhancement factor \(\beta_{\text{FN}}\) and the emitting area \(S_{\text{FN}}\) can be calculated for a given work function \(\varphi\). For simplicity, we have taken \(\varphi = 4eV\) (Nb), \(v(y) = t(y) = 1\), \(A = 154\) and \(B = 6830\) for \(E\) in MV/m and \(I_{\text{FN}}\) in A.

After FESM measurements the surface quality of the samples was investigated by means of a commercial optical profilometer (OP) with a lateral resolution of 2 μm as described elsewhere [9]. Further zooming into areas up to 98 μm² was achieved with an AFM in contact mode which can be positioned within ±2 μm of the OP results and has a lateral (vertical) resolution of 3 nm (1 nm). Using these results the linear and square roughness \(R_s\) and \(R_q\) of the surfaces can be calculated, and the geometric field enhancement factor \(\beta_{\text{geo}}\) of pronounced features can be estimated. Finally scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX) was applied to search for the EFE origin and foreign materials at the emission site within a correlation accuracy of ±100 μm.

Figure 1: Schematic view of the FESM [7].
Heat Treatments

For HT of the samples a resistive furnace located in the load-lock of the FESM (Fig. 1) was used which provides temperatures T up to 1200°C under HV conditions (≤10⁻⁶ mbar). T is measured with a thermocouple (Pt10Rh-Pt type S) and regulated by a commercial PID-controller (JUMO cTRON 04) within ± 1°C. The HT consist of a warm-up ramp from room temperature to the set point (≤ 6.3 °C/min), the annealing over time t and a natural cool-down phase, which can last up to 3h for T = 400°C.

In order to get useful steps after the usual cavity baking conditions (HT122), the required duration t of HT at different T can be estimated from calculations of the amount of produced oxygen atoms [10]:

\[ C_{ox} \alpha 1 - \exp\left(-k_{ox}(T) \cdot t\right) \]  

(2)

The oxygen is released from the conversion of the natural insulating Nb₂O₅ layer with an original thickness of d_{ox} = 64 Å [11] into the semiconducting NbO₂ and finally into the metallic NbO with the overall reduction rate [10]

\[ k_{ox} = A \cdot \exp\left(E_u / RT\right) \]  

(3)

(A = 3·10⁹ 1/s and E_u = 135 kJ/mol), C_{ox} was increased by one order of magnitude by choosing appropriate T and t until C_{ox} = 1 (HT325) with an additional HT at T = 400°C. XPS surface analysis of anodized and heated Nb samples [11], however, show that even at C_{ox} = 1 a thin Nb₂O₅ layer is still present on top of the Nb surface. In table 1 the graphically from [11] interpolated d_{ox} values are compared to the C_{ox} values. Probably this discrepancy can be explained by an incomplete diffusion of the produced oxygen atoms out of the oxide layer.

Table 1: Parameters of HT, values of C_{ox} calculated with (2) and (3), and d_{ox} taken from [11].

<table>
<thead>
<tr>
<th>HT</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>Warm-up time [h]</th>
<th>C_{ox}</th>
<th>d_{ox} [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>22</td>
<td>672</td>
<td>-</td>
<td>1.57·10⁻³</td>
<td>64.0</td>
</tr>
<tr>
<td>HT122</td>
<td>122</td>
<td>24</td>
<td>3</td>
<td>3.64·10⁻⁴</td>
<td>45.0</td>
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<tr>
<td>HT150</td>
<td>150</td>
<td>12</td>
<td>1</td>
<td>2.76·10⁻¹</td>
<td>39.4</td>
</tr>
<tr>
<td>HT175</td>
<td>175</td>
<td>9</td>
<td>1</td>
<td>1.75·10⁻²</td>
<td>34.5</td>
</tr>
<tr>
<td>HT200</td>
<td>200</td>
<td>8</td>
<td>1</td>
<td>0.101</td>
<td>30.0</td>
</tr>
<tr>
<td>HT250</td>
<td>250</td>
<td>10</td>
<td>1</td>
<td>0.971</td>
<td>20.7</td>
</tr>
<tr>
<td>HT325</td>
<td>325</td>
<td>6</td>
<td>1</td>
<td>1.000</td>
<td>11.0</td>
</tr>
<tr>
<td>HT400</td>
<td>400</td>
<td>2</td>
<td>1</td>
<td>1.000</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Samples

We have used two LG and two SC Nb (RRR > 250) samples with a diameter of 28 mm welded to a support rod. The samples were polished at DESY in two steps: 1. buffered chemical polishing (HF (48%): HNO₃ (65%): H₂PO₄ (85%), 1:1:2) up to 40 μm and 2. electropolishing (HF (40%): H₂SO₄ (98%) 1:9) up to 140 μm. Finally they were high pressure rinsed with ultrapure water, covered with dry-ice-cleaned protection caps (Fig. 2), sealed in plastic bags in a cleanroom class ISO5 and transported to Wuppertal. The protection caps were not removed until the samples faced at least high-vacuum conditions in the load-lock of the FESM and also used during transport to other measurement systems. The samples have two marks on the edge for correlated positioning in FESM, OP and SEM.

RESULTS AND DISCUSSION

Surface Quality

Survey scans (OP, 25×25 mm², 25 μm lateral res., (Fig 3a) showed that the surface of the samples is flat (≤2 μm) in the central areas (1 cm²). The mean roughness of the samples in these areas was Rₚ = 83 nm (Rₚ = 103 nm) for the SC Nb samples and Rₚ = 117 – 205 nm (Rₚ = 149 – 248 nm) for the LG Nb samples depending on the grain orientation. The AFM measurements (98×98 μm², 10 nm lateral res.) showed Rₚ = 8 nm (Rₚ = 10 nm) for SC Nb and Rₚ = 7 – 11 nm (Rₚ = 9 – 14 nm) for LG Nb. High resolution OP in small (1 mm²) selected areas (Fig. 3b) showed only few surface defects with low β_{geo} ≤ 6, e.g. strings of small pits as residues of scratches, and AFM profiles at the grain boundaries revealed only β_{geo} ≤ 4 (Fig. 3c). According to (1), geometrically caused EFE from these samples should not arise up to field levels of about 300 MV/m.

<table>
<thead>
<tr>
<th>EFE Statistics of HT Activated Emitters</th>
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<tr>
<td>The EFE of all samples was investigated in the central areas of 1 cm² before and after each HT as listed in table 1 (HT325 only on one LG, HT250 &amp; HT400 only on two LG and one SC). For the best sample shown in Fig. 4, no field activation was observed initially up to 160 MV/m, but a clear increase of N with increasing T demonstrates strong HT activation of emitters. The other three samples showed already few emitters at 100 MV/m before HT, but similar strong HT-activation effects, too. A dependency of the EFE on the grain boundaries or the crystal orientation of Nb could not be observed.</td>
</tr>
</tbody>
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Figure 2: Nb sample with protection cap.

Figure 3: (a) OP profile of LG sample (25 μm lateral resolution), (b) OP (2 μm lateral res.) and (c) 3D-AFM profile (10 nm lateral res.) of the grain junction.
In order to reduce the statistical error, the total number density of field- and HT-activated emitters on all four samples is shown in Fig. 5a. Obviously N(E_{act}) increases exponentially within error bars after all HT. The monotonous shift to higher N with T indicates that emitters on an annealed surface can be already activated at lower E_{act} than on initial Nb surfaces. Moreover, HT lead to emitters with E_{on} down to 40 MV/m (Fig. 5b), which are relevant for the ILC (E_{acc} = 31.5 MV/m, E_{peak}/E_{acc} = 2).

In Fig. 6a, the number density of emitters activated by each HT (N_{HT}) increases until C_{ox} = 0.975 (HT250), but a further raise of N_{HT} can be observed until HT400, which would demand a second activation process. In contrast, correlating N_{HT} with d_{ox} from table 1 (Fig. 6b) leads to a monotonous decrease with oxide thickness. Moreover it seems that the difference between E_{act} and E_{on} becomes smaller for HT400 (Fig. 5b). Therefore, higher T or longer annealing times might lead to an activation of all potential emitters at their final E_{on}.

**Single Emitter Characteristics**

SEM investigations of the 10 strongest emission sites selected from all field maps revealed 30% surface defects, 30% particulates and 40% destroyed or unidentified emission sites. EDX in regions with particulates and destroyed emitters showed W (probably from the anode), Al and Nb.

Surface defects mostly showed a FN-like I-V curve, often with nearly parallel slopes after different HT (Fig. 7). The resulting FN parameters are reasonable for this feature but differ significantly from the calculated $\beta_{geo} = 6$ resulting from the AFM profile. It is remarkable that E_{on} of this emitter varies non-monotonously with d_{ox} and the current is most unstable after HT200 and HT250. This reflects a rather complex structure of the remaining oxide at this defect.
In comparison, particulates like the one shown in Fig. 8 often reveal much more unstable IV-curves, which result in unreasonable FN parameters (e.g. $S_{FN} = 10^{11}$ km$^2$). Therefore, metal-insulator-metal or resonant tunnelling emission models should be considered for such effects [12].

![Figure 8: (a) unstable EFE ($\beta_{FN} = 5 - 140, S_{FN} = 10^{-7} - 10^{29}$ $\mu$m$^2$) of a melted Al particulate (b).](image)

### CONCLUSIONS AND OUTLOOK

The HT of LG and SC Nb leads to activation of remaining particulates and surface defects due to the dissolution of the natural insulating Nb$_2$O$_5$ layer. Activated surface defects show FN-like EFE with reasonable $\beta_{FN}$ and $S_{FN}$ values, which are difficult to be derived from AFM profiles and SEM images. Activated particulates reveal unstable EFE and other mechanism.

Air exposure (or anodizing) of the surface might deactivate such emitters. Furthermore high current processing or ion impact of emitters should be investigated.

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### REFERENCES