This week Program

- ❑ **Alternative Processes for bulk Nb Technology**

  Today, Monday 22 PM

- ❑ **SRF Materials Other than Bulk Nb**

  Tuesday 23 PM

- ❑ **RF, Cryogenic & Other Methods for SRF Materials**

  Wednesday 24 PM

- ❑ **Surface/Material Analyses for SRF Materials**

  Thursday 25 AM

USPAS June 2015 Rutgers

ALTERNATIVE PROCESSES FOR BULK NB TECHNOLOGY

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Thomas Jefferson National Accelerator Facility

Standard Nb Surface Treatments

From Last week …

Required Procedures for Qualifying SRF Cavities

- Degreasing surfaces to remove contaminates
- Chemical removal of exterior films incurred from welding
- Removal of damage layer of niobium from fabrication (150 µm)
- Removal of hydrogen from bulk Nb
- Mechanical tuning
- Chemical removal of internal surface for clean assembly (10-20 µm)

Additional "cleaning" steps if Electropolishing(EP) is used

- High Pressure Rinsing (HPR) to remove particulates from interior surfaces (incurred during chemistry and handling)
- Drying of cavity for assembly in cleanroom(reduce risk of particulate adhesion and reduce wear on vacuum systems)
- Clean assembly
- Clean evacuation
- Low-temperature baking

Conventional Surface Preparation for SRF Cavities

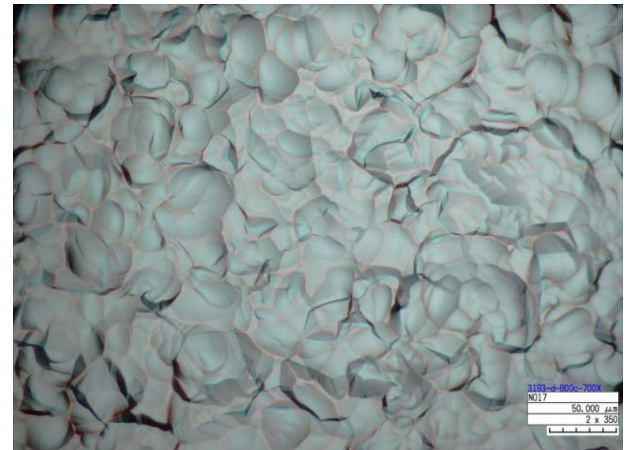
- **Buffered Chemical Polishing:** **$HF : HNO_3 : H_3PO_4$**

(ratio **1:1:1** or **1:1:2**)

HNO_3 : Oxiding agent

HF : Transforms Nb_2O_5 into a water soluble salt

H_3PO_4 : Reaction moderator or Buffer



- **ElectroPolishing**: **$HF : H_2SO_4$** (ratio **1:9**)

Both etching and EP electrolyte are composed of very harmful components both for humans and the environment, needing preventive and expensive mitigation procedures
Efforts around the world to get rid of the most harmful components

Alternatives to BCP

Standard BCP: $HF : HNO_3 : H_3PO_4$

Modified BCP: $HF : HNO_3 : H_2SO_4$ **(ratio 1:1:2)** at 78°C

Y. Uzel, K. Schnitzke, N. Krause: Appl. Phys., A30 (1983) p.185

$HF : HNO_3 : H_2SO_4$ **(ratio 1:1:1)** RT

C. Z. Antoine, A. Aspart, J.P. Charrier, H. Safa, B.Visentin, Proc 9th Workshop on SC RF, (1999) Santa Fe

Introduction of LESS HAZARDOUS COMPONENTS in the standard BCP

For example:

$HF \longrightarrow NH_4F$

$HNO_3 \longrightarrow H_2O_2$

$NH_4F + HCl + H_2O_2 + H_3PO_4$ at room temperature

Several percentages studied, the best results were obtained with the

$NH_4F : HCl : H_2O_2 : H_3PO_4$ in the 2:2:4:1 ratio with (60g/l) of NH_4F

V. Palmieri, F. Stivanello, C. Roncolato, M. Valentino –Proc. 10th SC RF workshop, 2001 Tsukuba

Alternatives for EP: lactic acid

Improved Methods for Electrochemical Polishing of Nb Superconducting cavities
V.M. Efremov, L.M. Sevryukova, M. Hein, L. Ponto

2° International TESLA Workshop, DESY, Hamburg ,August 1991

Composition HF : H_2SO_4 : Lactic acid in the ratio 18 : 21 : 61

Current Density = 90-110 mA/cm^2
Voltage = 15-18 V
Temperature = 50-60 °C

Note: Lactic acid solutions can be explosive

Buffer Electro-Polishing (BEP)

Buffered Electropolishing (BEP) uses an acid mixture of lactic, sulfuric, hydrofluoric acids as electrolyte. Partial replacement of sulfuric acid by lactic acid makes handling the electrolyte safer.

Before BEP

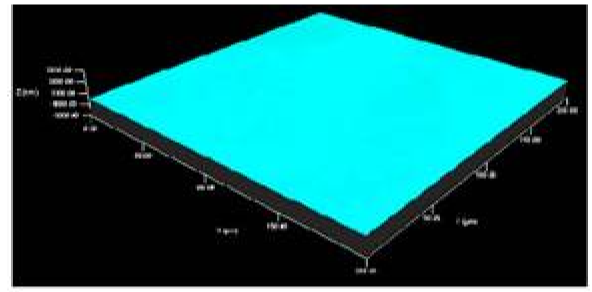
After BEP for 30 Minutes

Major Benefits:

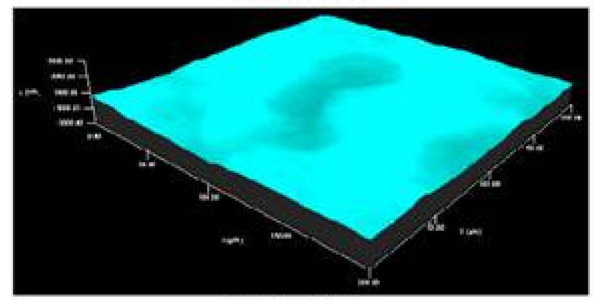
1. Smoothest surface finish
   BEP 35nm vs BCP 1274nm
   → better RF performance
2. Highremoval rate
   BEP 4.09µm/min vs. EP 0.38µm/min
   → potential huge reduction in cavity preparation cost

Current Status:

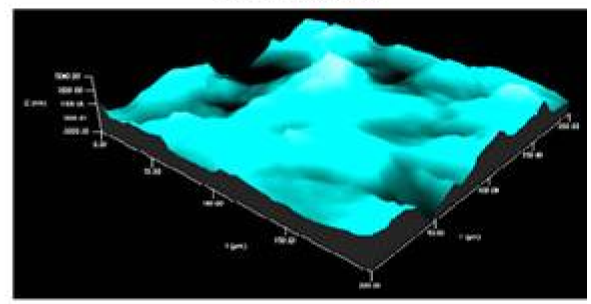
1. BEP on large grain cavity reaches 32MV/m
2. BEP on regular fine grain cavity reaches 23MV/m (quench limited)
3. The inner surfaces of cavities look very smooth for both large and fine grain cavities after BEP
4. Next, compare with standard EP



BEP RMS 35nm



EP RMS 251nm



BCP112 RMS 1274nm

Alternatives for EP: getting rid of HF?

There are a lot of horror stories about HF:

Hydrofluoric acid is a highly corrosive solution

If it is accidentally released, it forms an aerosol acid cloud which can cause serious bone damage and death by burns to the skin, tissue or lungs. Even minor exposure can cause skin burns and blindness.

A plethora of devastating histories in refineries using Hydrofluoric acid

- On contact, HF passes through skin and tissue.
- Contact with HF does not cause immediate pain, so systemic poisoning begins before the person is aware
- Because its action can be delayed for many hours, it can distribute through out the body, causing the erosion of bones.
- F-ions bind to Ca^{++} and Mg^{++} ions to form in soluble salts
- (CaF_2 and MgF_2 salts form some natural gemstones).
- In the body, Ca and Mg ions are used to mediate a variety of physiological processes, such as muscle movement.
- Cardiac arrests have been reported from concentrated acid burns to as little as 2.5% of exposed body surface area

The Chemical/Electro-chemical Polishing of 20,000+ cavities for ILC would require several hundred Tons of HF

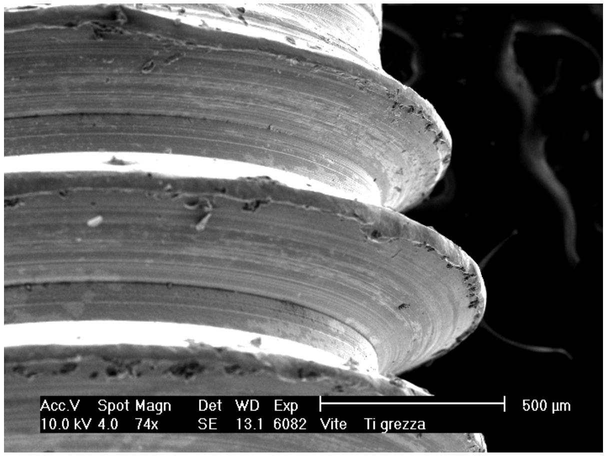
Phasing out the use of HF and enacting a safer alternative would be a big asset

EP Alternative: Ionic liquids

Ionic liquids are defined today as liquids which solely consist of cations and anions and which by definition must have a melting point of 100 °C or below.

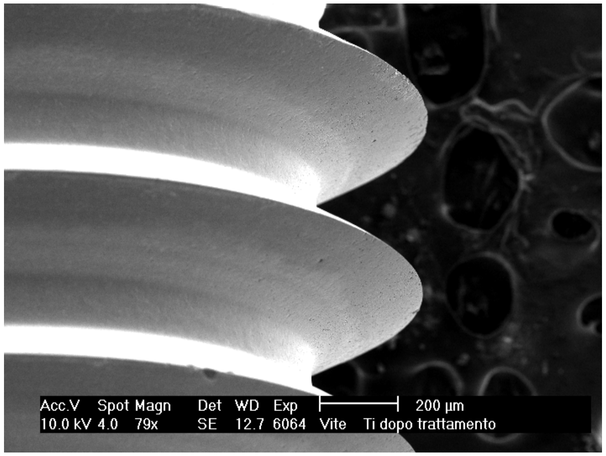
In the middle of the 1990s the term ‘‘room temperature molten salt’’ was definitely replaced by ‘‘ionic liquid’’.

The ‘‘room temperature molten salts’’ were regarded as uncommon and as a curiosity for a while. The situation has changed dramatically throughout the recent 3 years



Ionic liquids are going to represent a main stream in various fields of chemistry and physical chemistry!

Imagine making a liquid just by mixing two solids! And think what you could do with this liquid if it was non-toxic, biodegradable and could dissolve a wide range of materials.



The trend is to look for liquids that can be used to substitute the strong and corrosive acids traditionally used as solvents in many industrial chemical reactions.

Electropolishing solutions based on Ionic Liquid Technology

In exactly the same way as common salt, liquid salts consist of positively charged and negatively charged ions, though they are not simple ions like sodium and chloride but are much larger and more complex, and unable to form easily a crystal lattice. If even a small amount of heat is applied to them, the solid crystalline structure disintegrates and the bonds between the ions are broken. The salt becomes a liquid – an ionic liquid.

Benefits

- Non-aqueous
- Non-volatile
- Non-toxic
- Highly conducting
- Improved current efficiencies
- Recyclable
- Decrease hydrogen evolution
- Decreased emissions
- Iron Residue Recovery
- Costs comparable to organic solvents
- Bacterial growth inhibition
- Micro finish enhancement
- Reduced occurrence of intergranular attack (preferential etching)
- Reflective finish
- Polished surface can withstand cleaning and autoclaving
- Any size metal can be electropolished

Salt flats in California: A lake has evaporated, leaving behind a layer of salt.

HF-free electropolishing

Choline Chlorine enhances and accelerates growth in animals during times of rapid development (common poultry feed additive).

Choline is important for

- fetal development and for babies/children. Human milk contains high amounts of choline.
- cell membrane structure, for synthesizing folic acid and vitamin B12, and for protecting the liver from accumulating fat. (Take choline chloride supplements to protect the liver from damage, to lower cholesterol, to improve memory, to preserve prostate and to enhance mood!)

The brain has a voracious appetite for choline.

Choline is required for

- synthesis of the key neurotransmitter acetylcholine
- building and maintaining brain cell membranes.

(Acetylcholine is vital for thought, memory and sleep, and is also involved in the control of movements)

…. and to electropolish Niobium

Dosage and Use
Take 1 to 3 teaspoons daily.
It is best mixed with approximately
2 oz. of juice per teaspoon.

Electropolishing with Choline Chlorine

Molecular formula	$C_5H_{14}ClNO$
Molar Mass	139.62 $g.mol^{-1}$
Appearance	White or deliquescent crystals
Molecular Formula	302 °C (decomposes)
Solubility in water	very soluble

Choline chloride (2-hydroxyethyl-trimethylammonium) is a quaternary ammonium salt also known as Vitamin B4. It has a Choline cation with a Chloride anion.

It forms with Urea a Deep Eutectic Solvent able to dissolve many metal salts

ABBOTT Patent deposited by Shonix

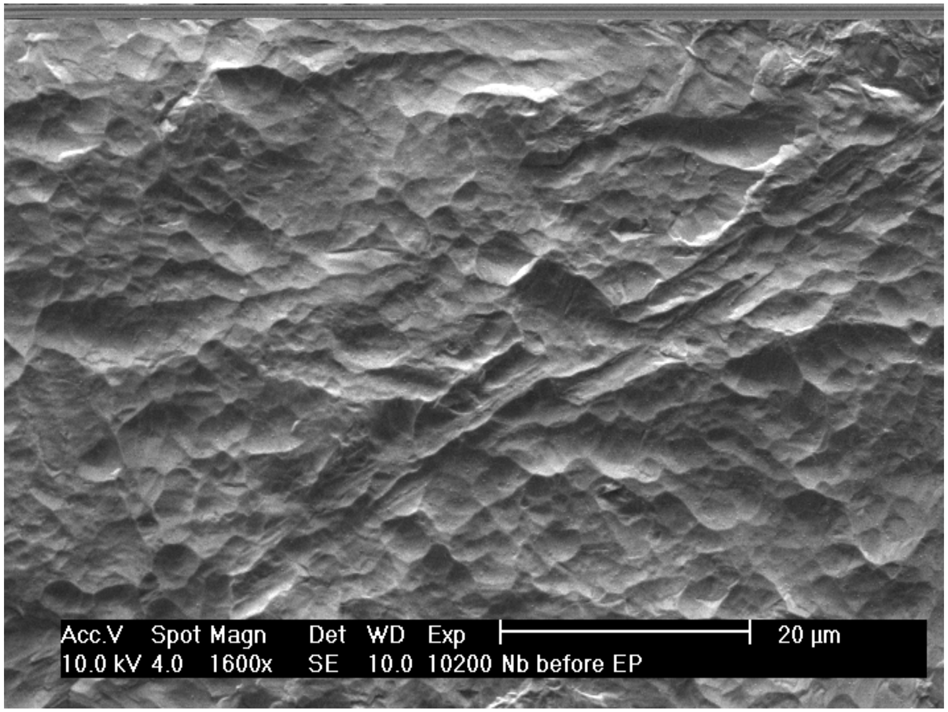
Surprisingly, however, we have now found that by forming the anion of an ionic compound from a hydrated metal salt and the cation from certain specific amine salts, it is possible to produce compounds which are liquid at low temperatures (i.e. 50 °C and below), relatively inexpensive, and relatively water insensitive.

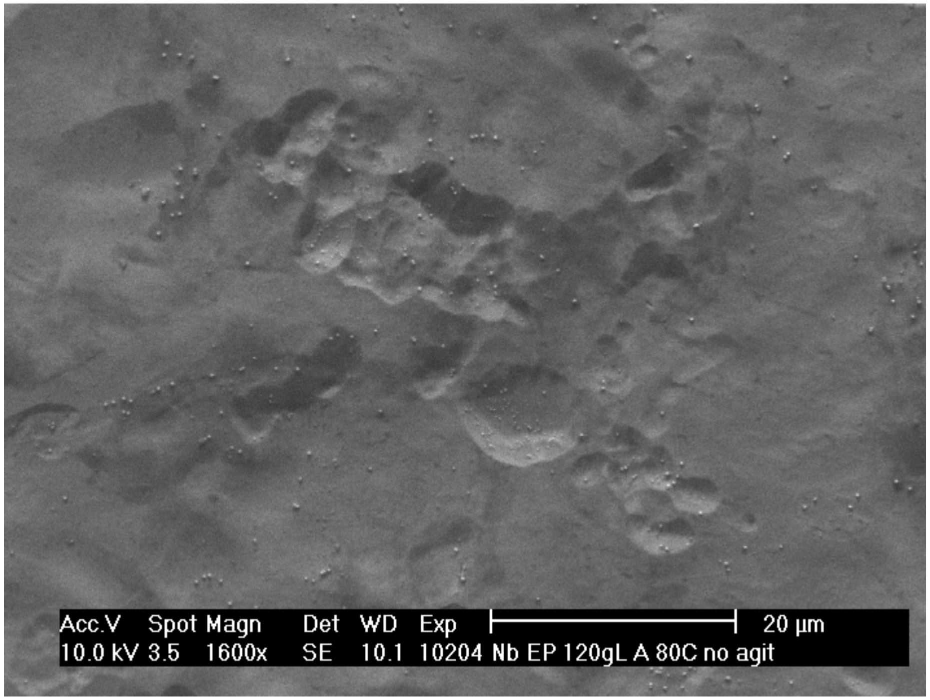
Choline chloride and hydrated metal halides, as magnesium chloride, Copper nitrate, or Calcium chloride, … succeed in electropolishing a big variety of metals.

A. P. Abbott et al., Electrochemica acta 51 (2006) 4420-4425

On the basis of Abbott Patent

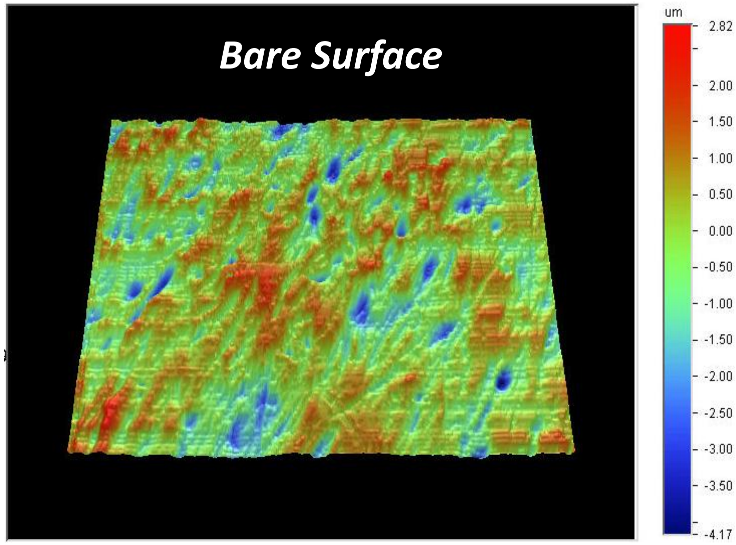
Electropolishing of Nb was achieved by a mixture of Choline Chloride, Urea, NH_4F at 80°C.





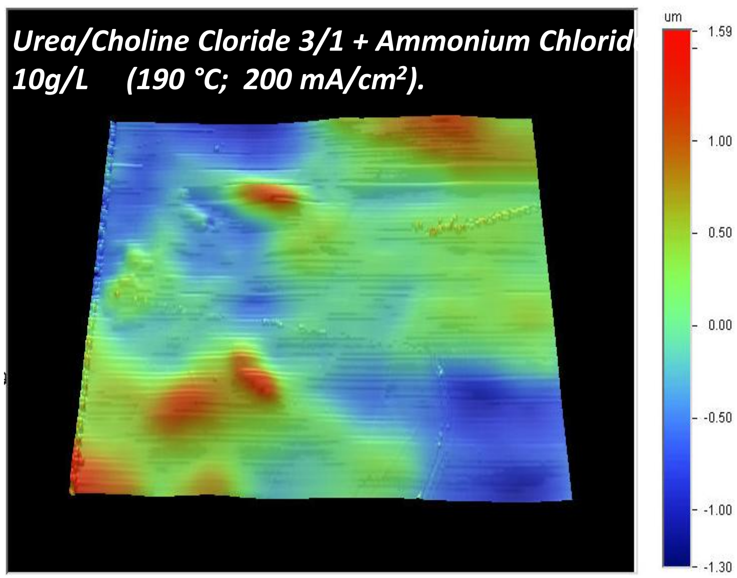
Profilometry (500mm x 500mm scans)

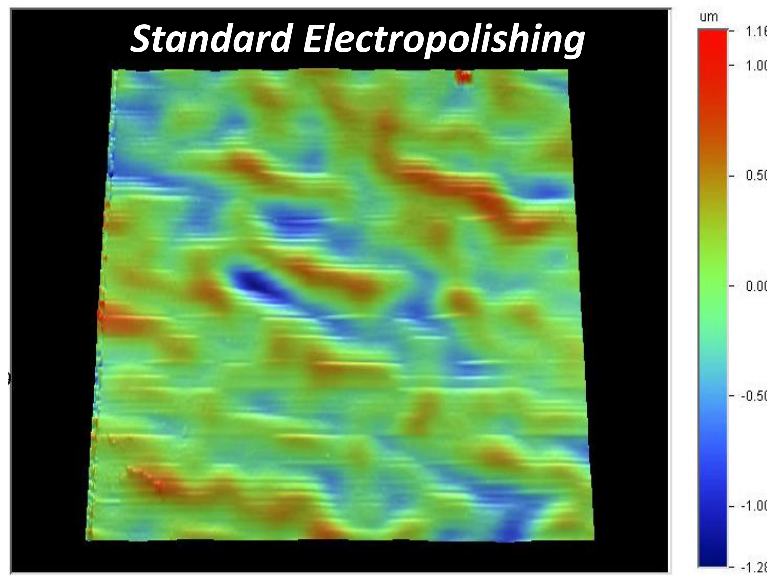
R_a= 785.9 nm



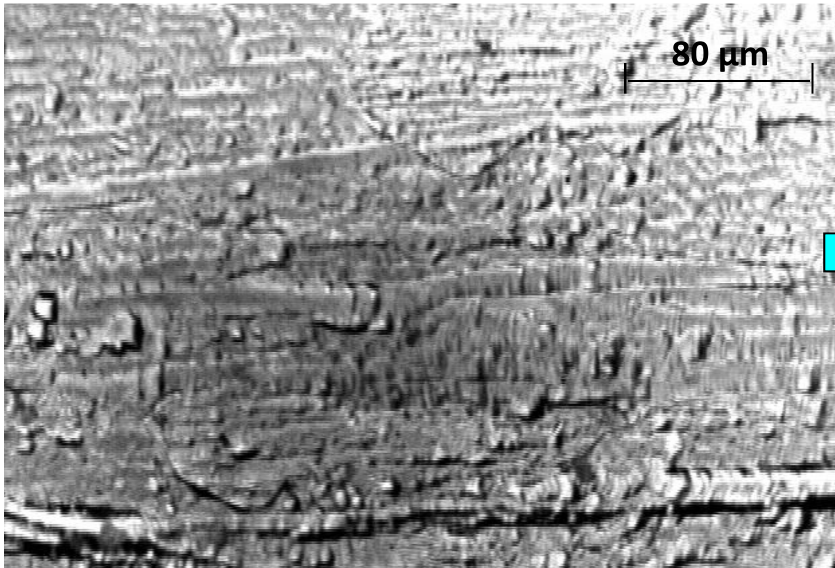
R_a= 248.8 nm

R_a= 189.7 nm

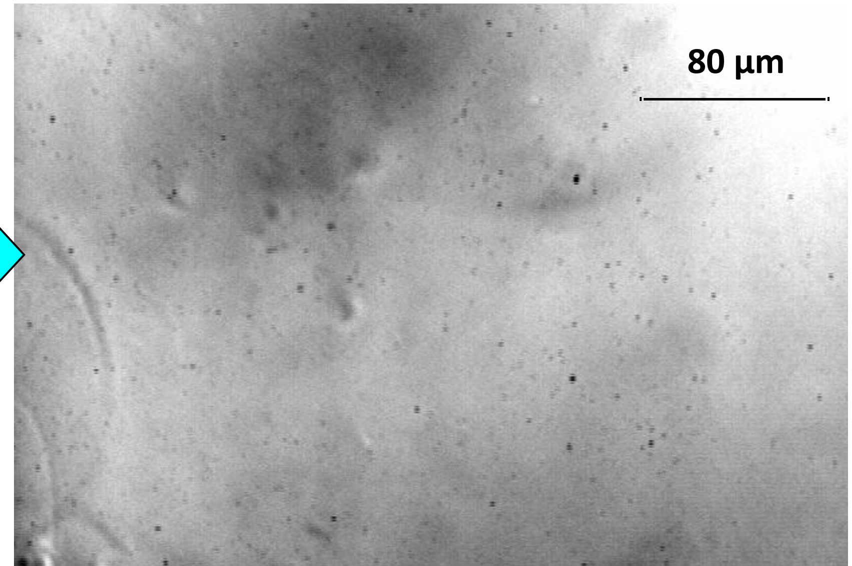




Optical Microscopy



As received surface



Urea/Choline Chloride 3/1 + Ammonium Chloride - 10g/L (190 °C; 20 mA/cm²)

- ***Best Recipe***

  Urea/Choline Chloride 3/1

  + Ammonium Chloride (NH_4Cl) *10g/L (190 °C; 200 mA/cm²).*

Application to Cavities still in progress

BIPOLAR OR PULSED REVERSE EP

Bipolar Pulse EP for Nb SRF Cavity

Bipolar EP (pulse-forward, reverse-pulse technique) uses an **anodic forward pulse** to grow an oxide layer on the reacting surface. The anodic pulse is followed by a delay, or voltage off-time, that dissipates the heat, removes reaction by-products, and replenishes active agents needed for the reaction. A cathodic pulse then reverses the voltage and reduces the passive oxide layer on the reacting surface.

Anodic Pulse "Tuned" to:

- **Control current distribution**
- **Eliminates need for viscous, low water content electrolytes , such as H_2SO_4[1], NaOH[2]**

Cathodic Pulse "Tuned" to:

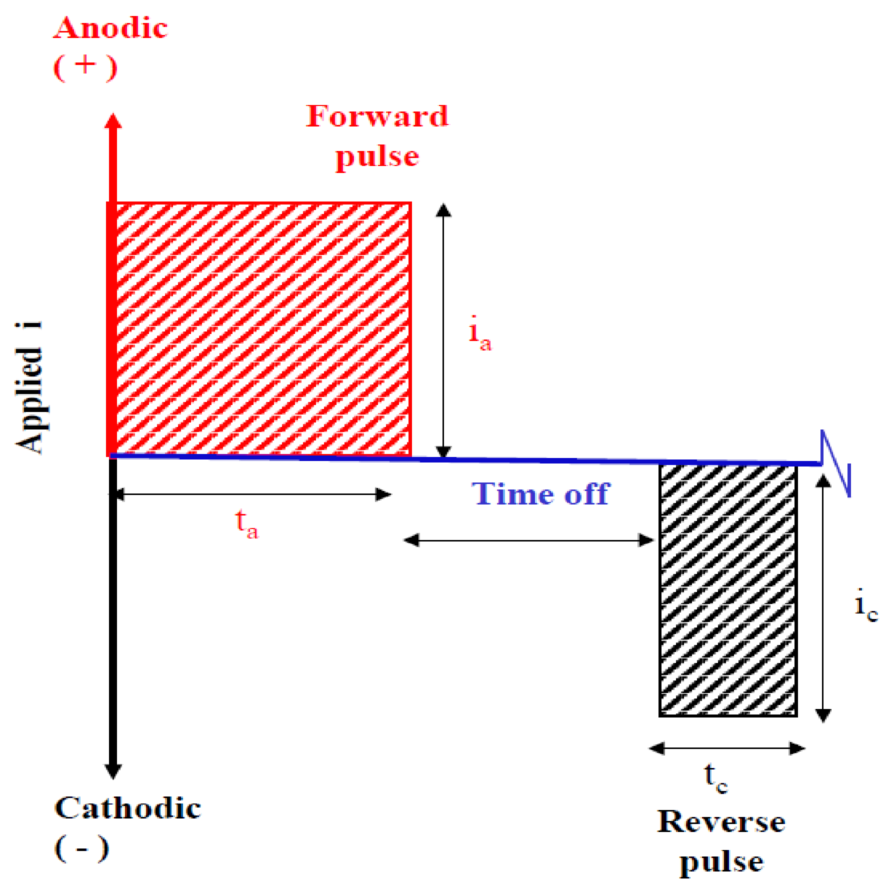
- **Reduce oxide/depassivate surface**
- **Eliminate need for HF**

Need further understanding

Off-Time "Tuned" to:

- **Heat dissipation**
- **Replenish reacting species**
- **Remove reaction products**

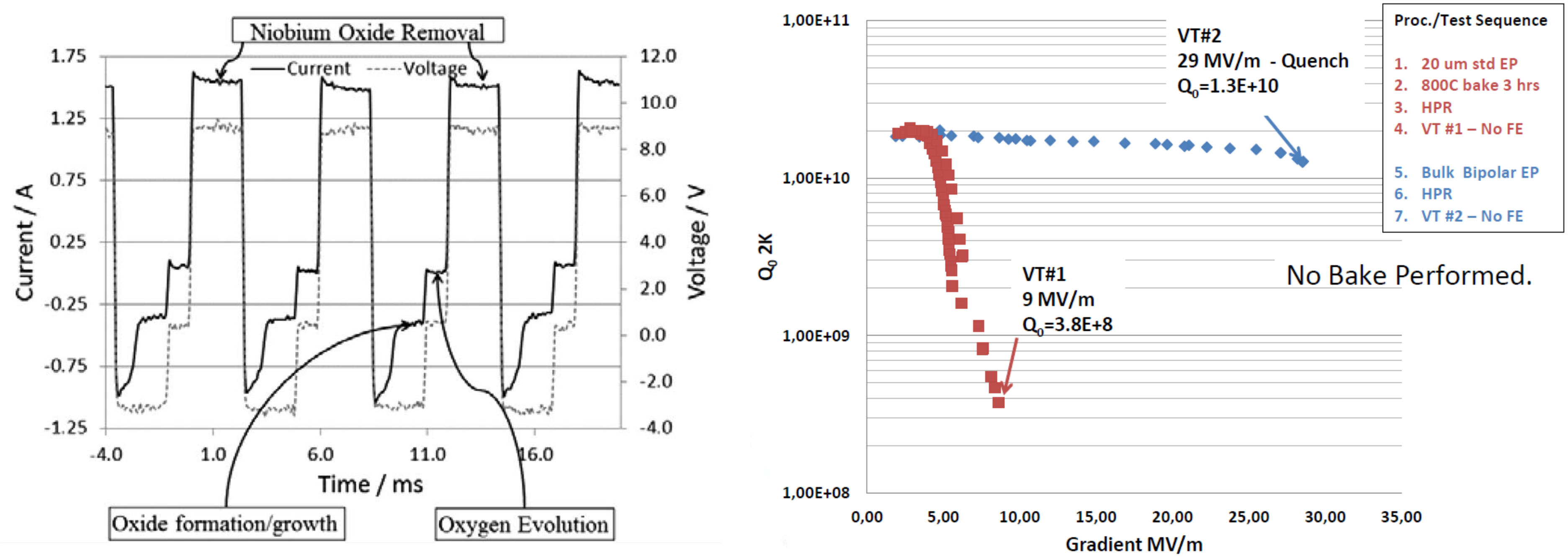
Need further optimization



1) M. Inman, E. J. Taylor, and T. D. Hall *Journal of The Electrochemical Society*, **160** (9) E94-E98 (2013)

2) M. Umehara, T. Saeki, H. Hayano, LINAC 2014

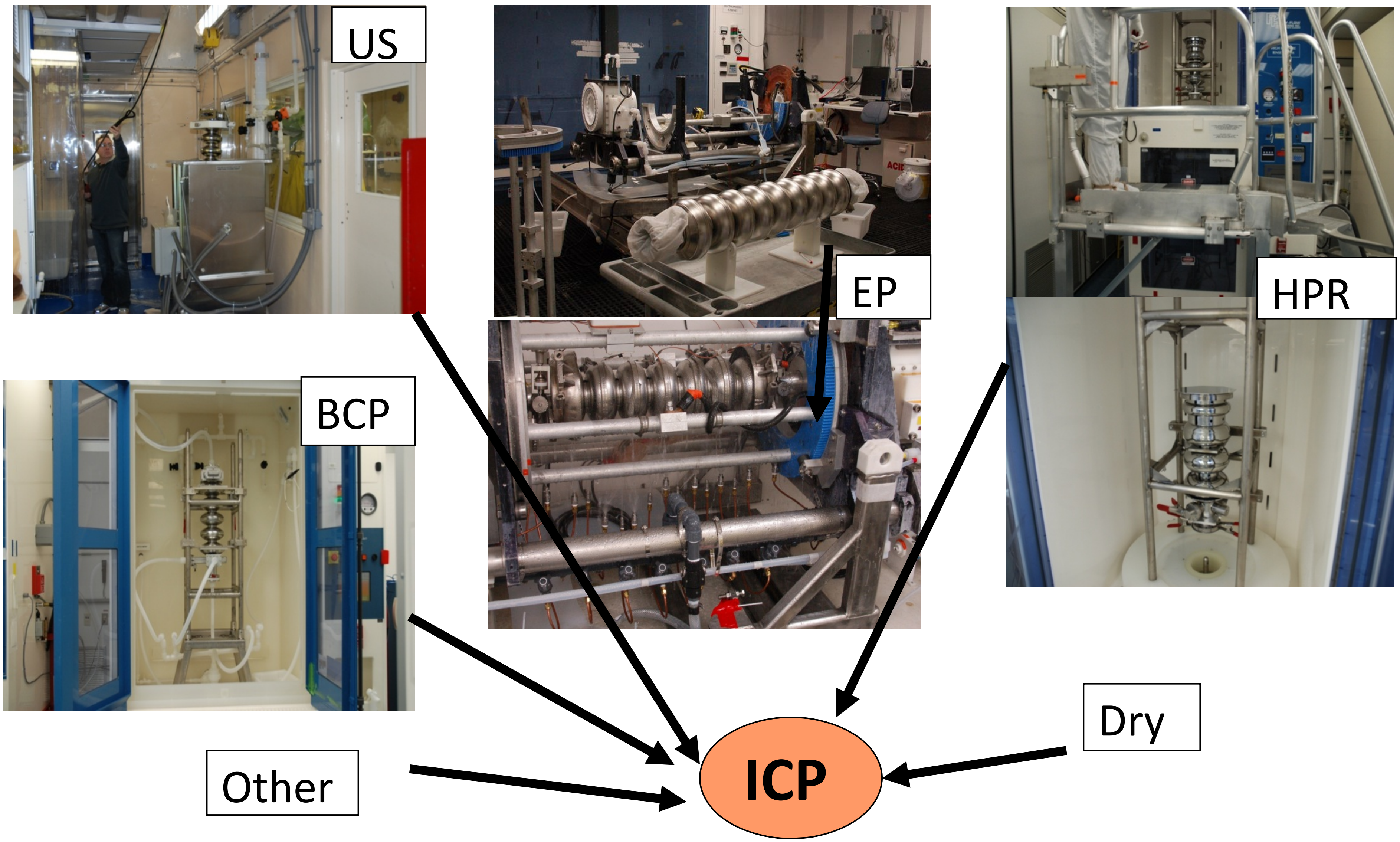
Pulse Reverse EP was successfully transitioned to single cell SRF cavities



- Bipolar reverse EP, using a dilute aqueous H_2SO_4 electrolyte without HF, yields equivalent RF performance with traditional EP.
- It is ecologically friendly and relatively benign electrolyte options for cavity processing exist
- It needs to be developed for multi-cell cavities

M. Inman, E. J. Taylor, and T. D. Hall *Journal of The Electrochemical Society*, 160 (9) E94-E98 (2013).
Allan Rowe, TUIOCO2, SRF2013. Paris, France

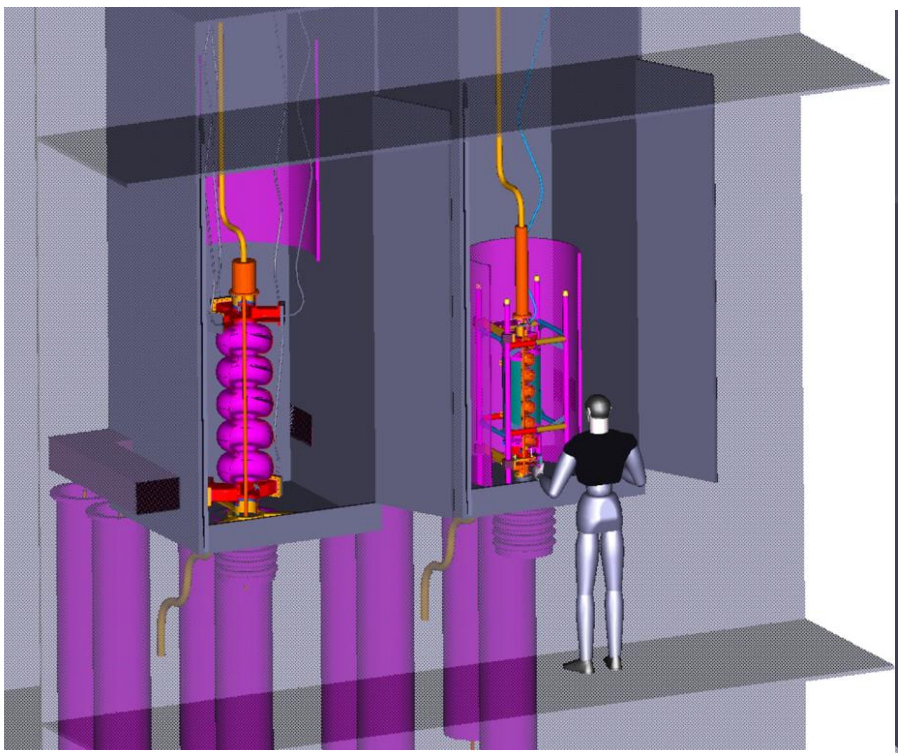
ICP (Integrated Cavity Processing) Concept will integrate multiple process steps with minimum handling - future SRF Cavity process tool

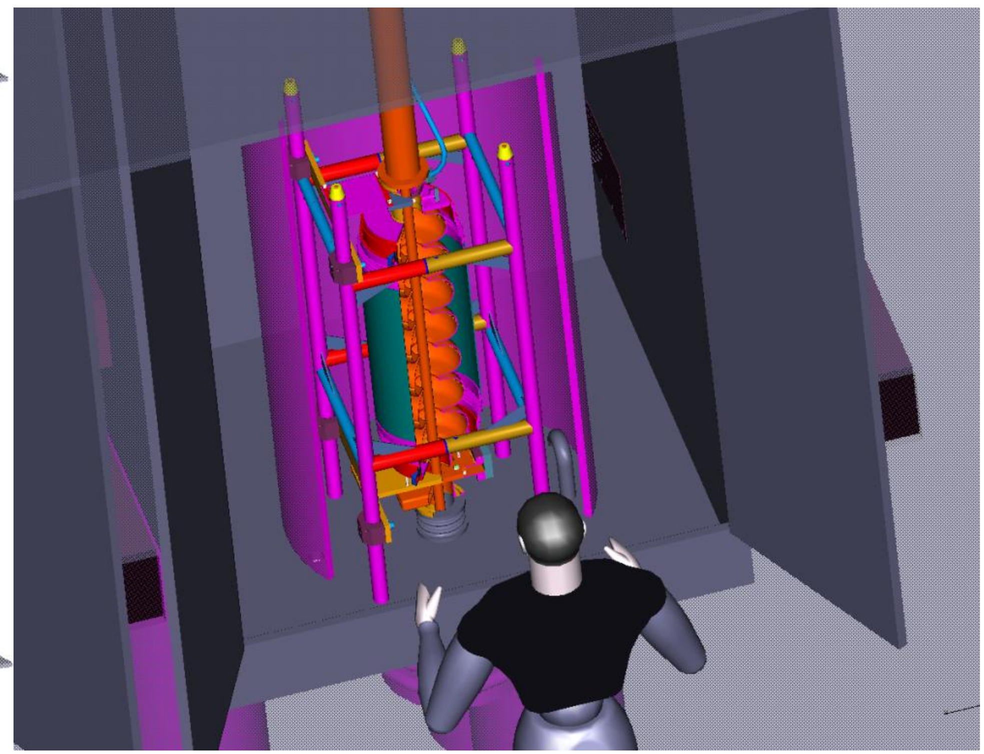


The next step, ICP

We need confident <u>and</u> variable multi-parameter process control.

- ICP units will integrate VEP, BCP, HPR, US, and HWR in an automated tool in a clean environment.
- The concept is to leave the cavity stationary and bring the sequential processes to the cavity.





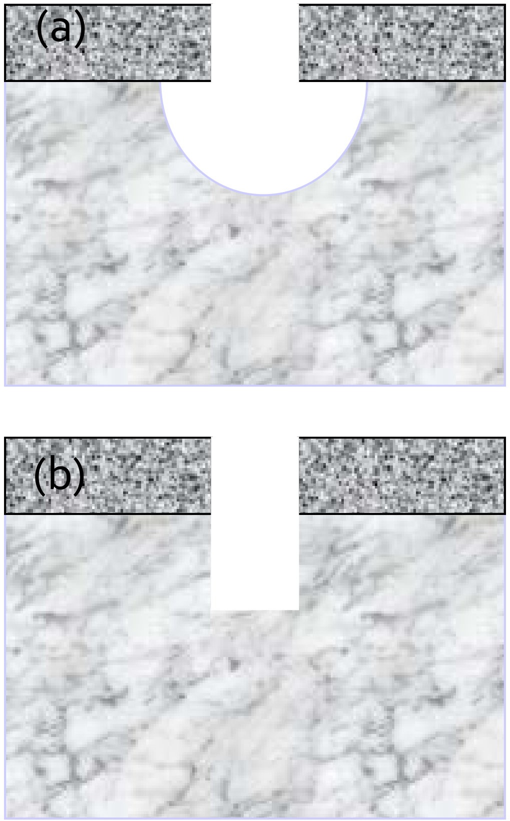
DRY ETCHING

Dry Etching vs. Wet Etching

Although Wet acid etching (BCP or EP) is the commonly used process in processing of SRF cavities, it has been abandoned as the fabrication process in microelectronic industry, primarily due to the isotropic material removal

Plasma-assisted etch process (dry etching) is the enabling process in semiconductor industry, since it can be highly selective with respect to direction and hence indispensable in patterned removal of surface material or in removal of material from non-flat surfaces .

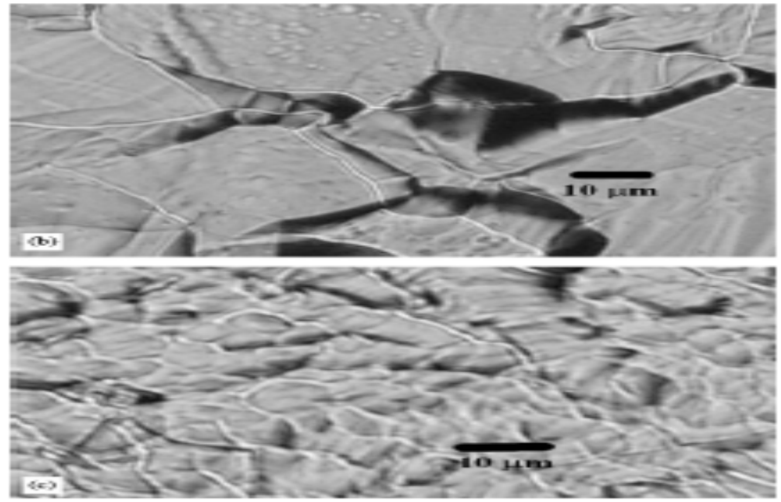
Schematic illustration of
(a) isotropic action (wet) etching,
and (b) anisotropic (dry) etching



Motivation for dry etching for SRF cavities

Comparison of surface micrographs taken with KH-3000 digital microscope with magnification 10×350

M. Rašković, L. Vušković, S. Popović, L. Phillips, A. M. Valente-Feliciano, S. B. Radovanov, and L. Godet, Nucl. Instrum. Methods Phys. Res. A **569**, 663 (2006



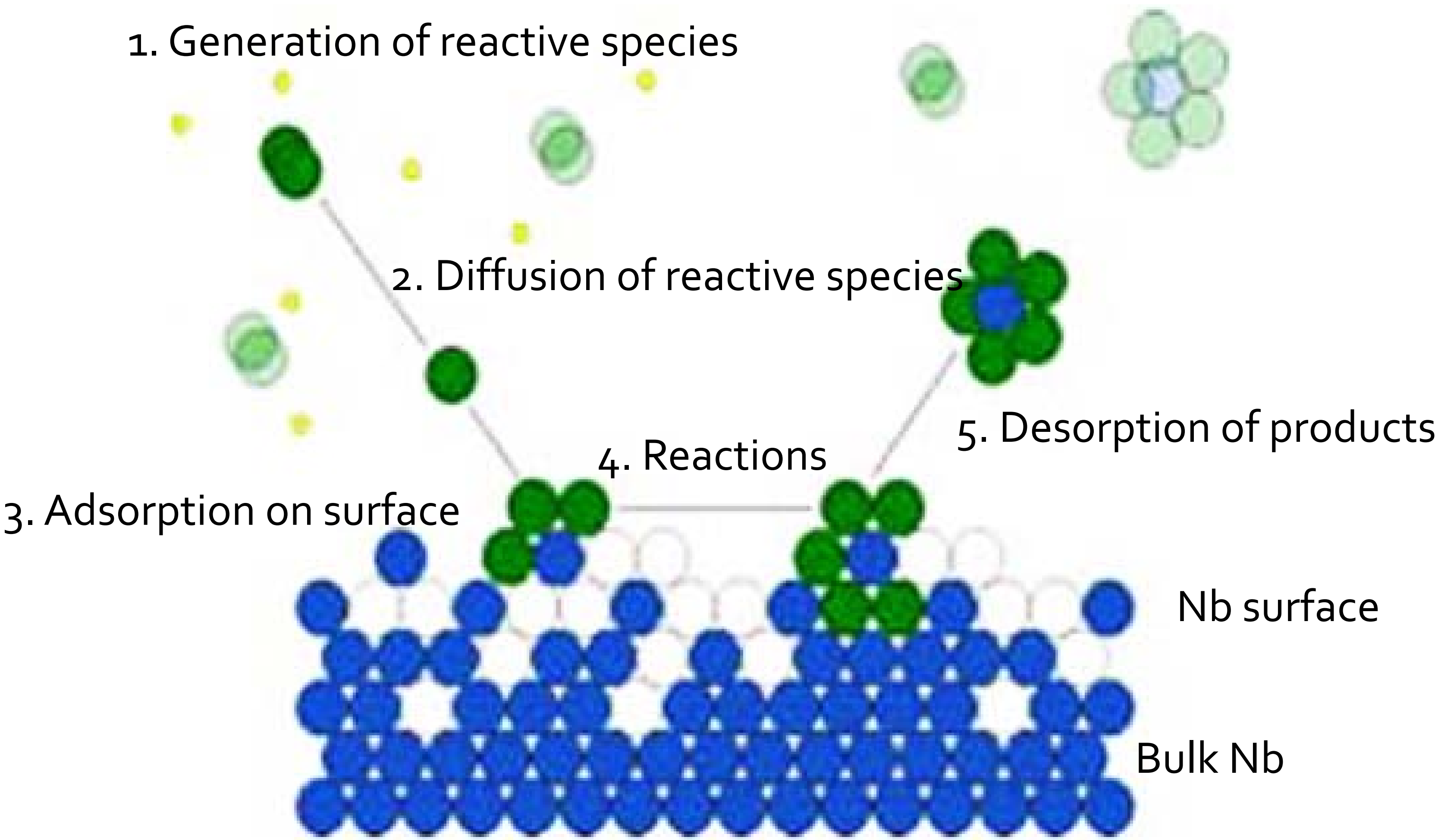
BCP Process

Dry Process

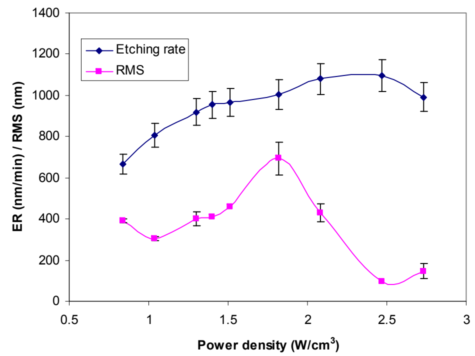
- Low Cost
- No wet chemistry
- Environment and People friendly (compared to wet etching process)
- **Full control on the final surface**
    - "Oxide –free" surface if kept under UHV
    - A variety of surfaces can be intentionally created through plasma processing
        - ✓ Pure Nb_2O_5, or other cap layer
        - ✓ superconducting NbN
        - ✓ S-I-S Multilayer

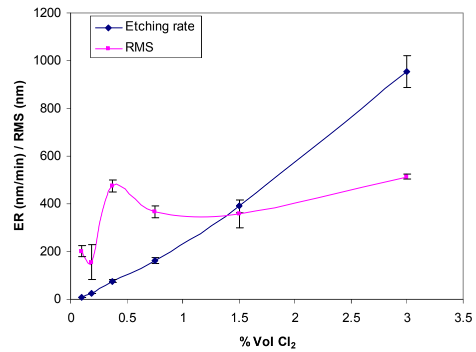
Mechanism of Plasma Etching

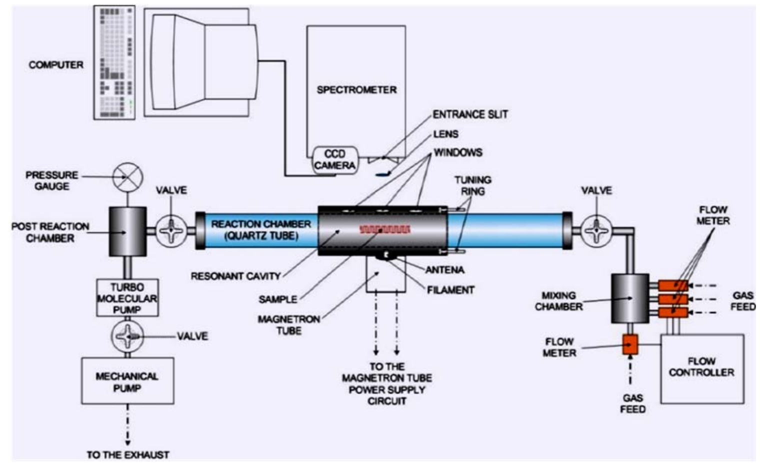
$2Nb\ (s) + 5Cl_2\ (g) \longrightarrow 2NbCl_5\ (g)$ No oxidizing agent needed



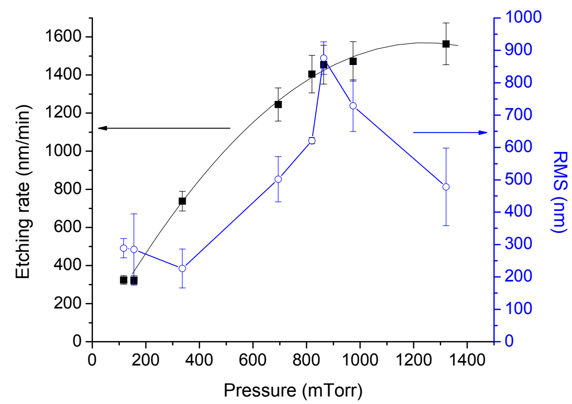
Plasma etching of Nb surfaces (small samples)







M. Rašković, S. Popović, J. Upadhyay, and L. Vušković, L. Phillips, A. M. Valente-Feliciano, "High etching rates of bulk Nb in Ar/Cl_2 microwave discharge," J. Vac. Sci. Technol. A. 27 (2), 301 (2009)

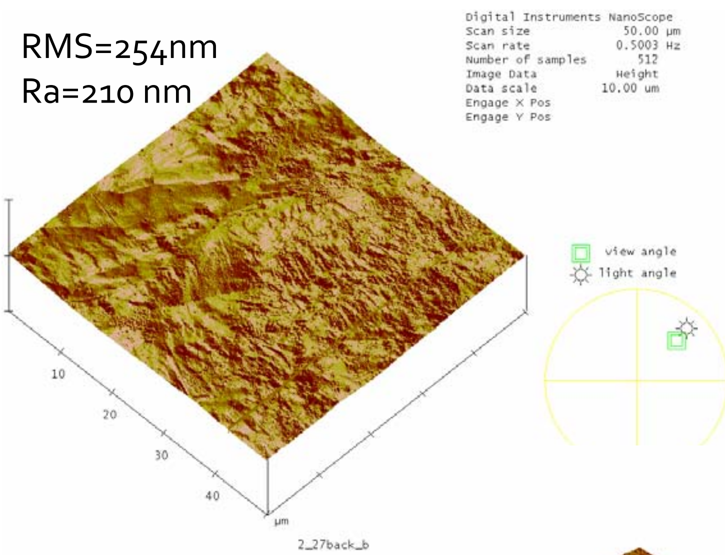


Small Nb samples etching in a microwave plasma at 2.45 GHz inside a quartz tube
Etching rates up to 1.7 µm/min for 97% Ar and 3% Cl gas mixture.
Surface roughness of plasma etched sample was equal or lower than the chemically etched samples.

Flat Samples - Surface Roughness

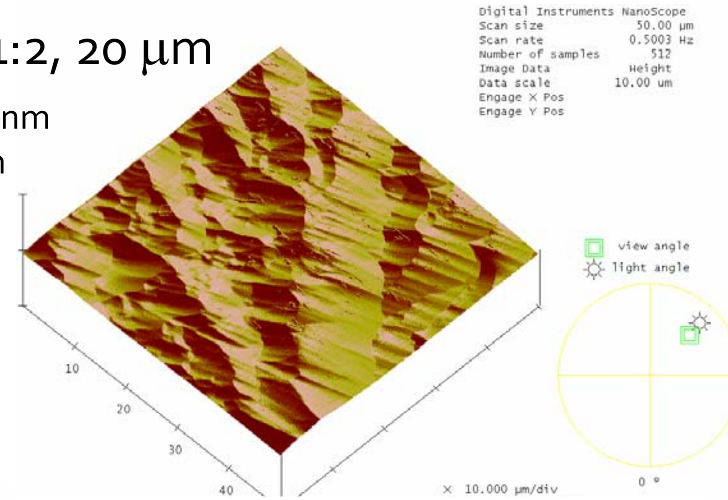
As received

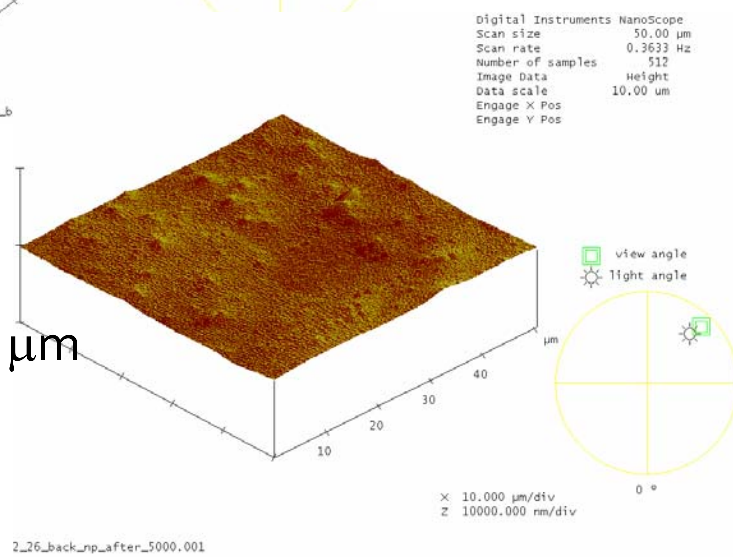
RMS=254nm
Ra=210 nm

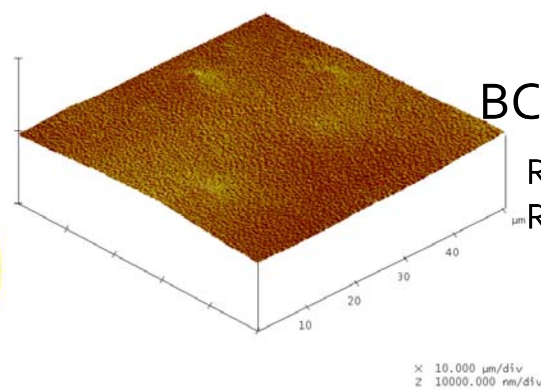


BCP 1:1:2, 20 µm

RMS =286nm
Ra=215nm







BCP + PE

RMS =215nm
Ra=169 nm

3-steps PE ,120 µm

RMS=234nm
Ra=174 nm

120 µm

AFM scans (50 µm × 50 µm)

Plasma Etching of Single Cell Nb Cavity

3-step process

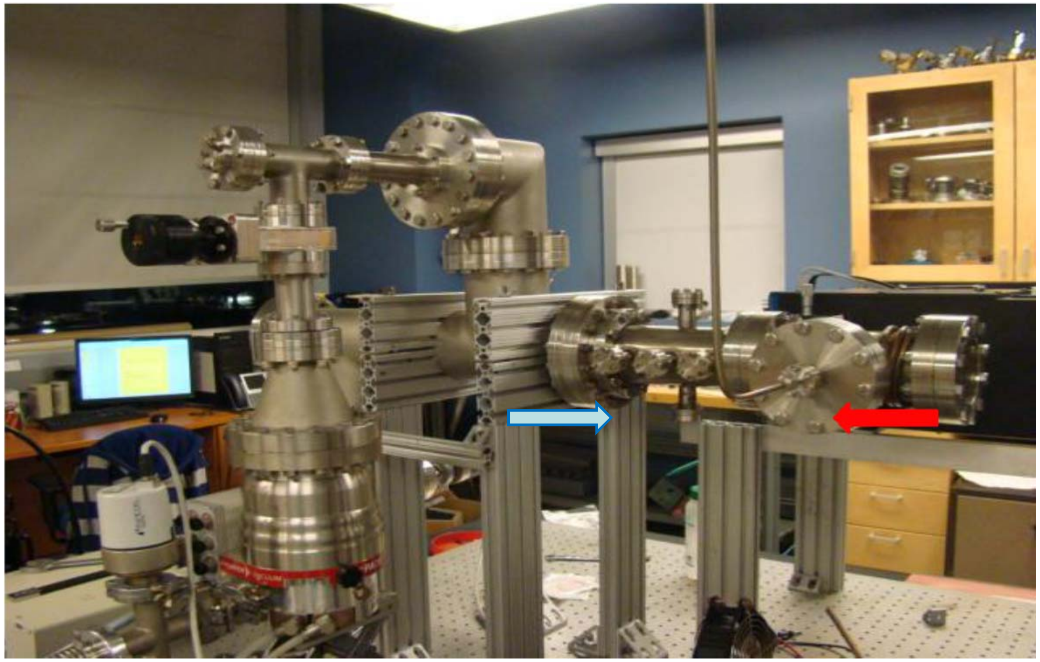
1. **Pure Ar** ⇨ removes physisorbed gasses and organic residues from Nb surface without damaging surface
Time 30 min, Total flow 150 sccm, Input power density 2.08 W/cm^3 ,Pressure 500 mTorr
Etching rate 0nm/min

2. **3 Vol% Cl_2 in Ar** ⇨ removes surface necessary for cavity production
Time 120 min , Total flow 198.6 sccm, Input power density 2.08 W/cm^3 , Pressure 550 mTorr
Etching rate 1 μm/min
removes ~120 mm of surface in 2 h

3. **1.5 Vol% Cl_2 in Ar** ⇨ removes surface under conditions more favorable for surface smoothening
Time 240 min , Total flow 348.6 sccm, Input power density 1.4 W/cm^3 , Pressure 1250 mTorr
Etching rate 0.5 μm/min

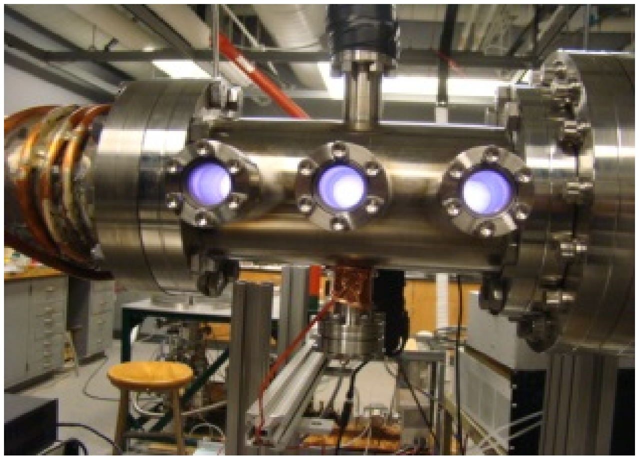
Transition from planar to cylindrical geometry

- **Investigate the plasma etching behavior on samples placed on actual geometry of the single cell cavity (plasma distribution, roughness uniformity.. .)**
- **Plasma etching of single cell cavities and RF performance measurements.**



Schematic Diagram

Cylindrical plasma etching for Nb cavities

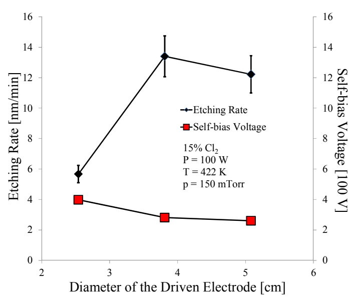


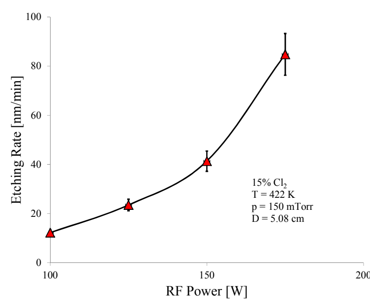
Transition from planar to cylindrical geometry

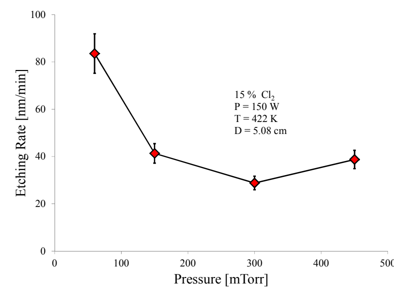
Coaxial capacitively coupled RF plasmaon large area curved Nb samples

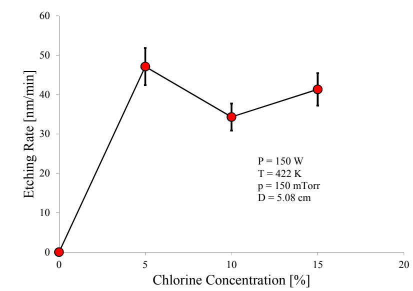
Study of the effect of discharge asymmetry by correlation of the inner electrode diameter with the self-bias voltage and the etching rate.

Determine the dependence of etching rate on the driven electrode diameter, RF power, gas pressure, and Cl concentration (at 422 K).









Robust etching of a cylindrical Nb sample of diameter comparable to cavity wall dimensions

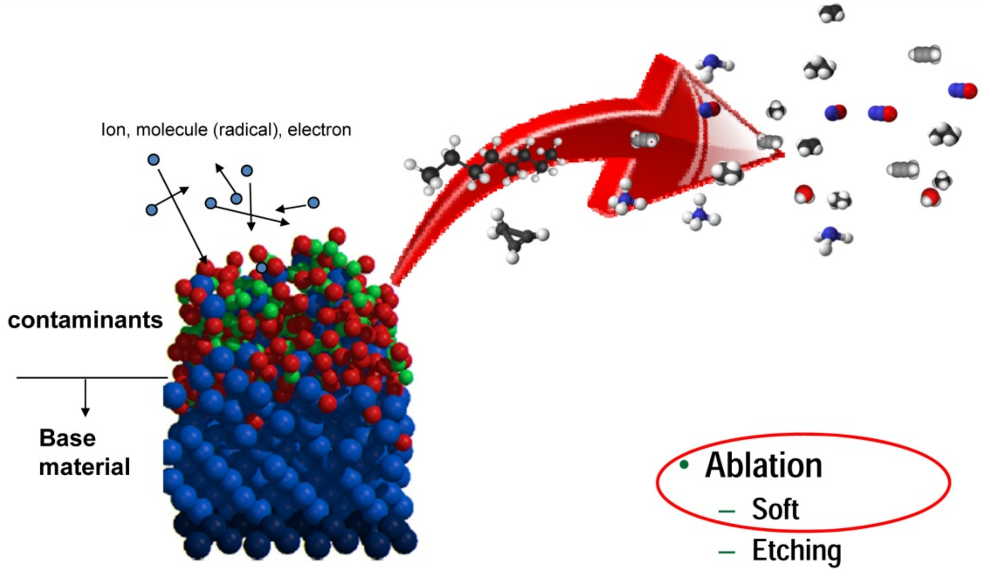
Plasma etching of a single cell Nb cavity : first results under analysis

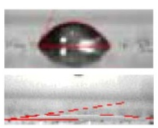
Old Dominion University

Plasma Etching of bulk Nb

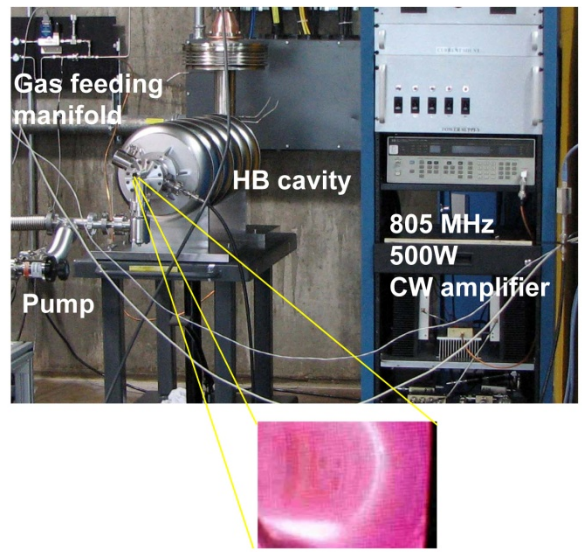
- Etching rates of bulk Nb as high as 1.7 ± 0.2 mm/min can be achieved in a microwave glow
- Discharge using Cl_2 as the reactive gas.
- Nb etching rate depends on Cl_2 reactive gas concentration and discharge parameters: input power density and pressure in reaction chamber.
- Surface composition analyses (EDS, XPS) show that no impurities have been introduced into Nb during microwave discharge treatment.
- Developed 3-step process.
- Further improvement needed to achieve the state-of-the-art roughness values of conventional EP.
- Emission spectroscopy result combined with measured etching rates, suggests that the Nb etching mechanism in Ar/Cl_2 MW glow discharge is more a chemical etching than a physical sputtering process.
- Final surface modifications (final oxidation, nitridation…) can be done in the same process cycle with the plasma etching process.
- The geometry of the inner surface of the cavity implies that the plasma discharge has to be asymmetric. ca

Atmospheric plasma cleaning for cavities processing





- Ablation
  - Soft
  - Etching
- Activation
- Crosslinking
- Deposition



First plasma in the SNS HB cavity

300W forward
200W reflected
1e-4 torr

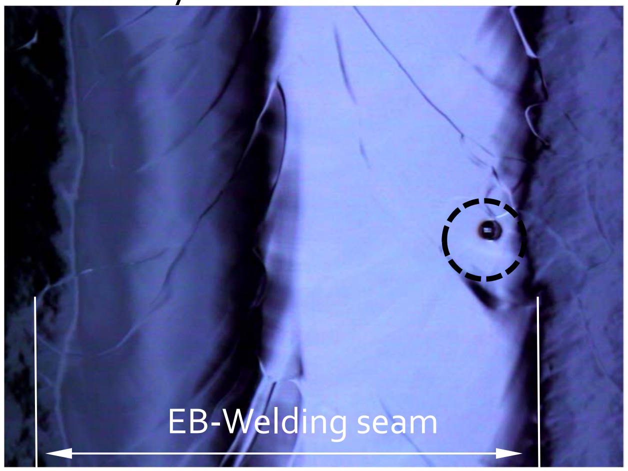
Atmospheric plasma experiments going on at SNS, FNAL, INFN-LNL

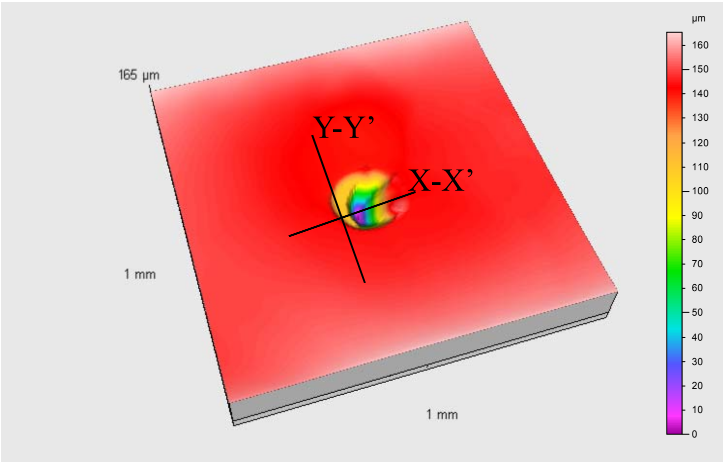
SURFACE MELTING

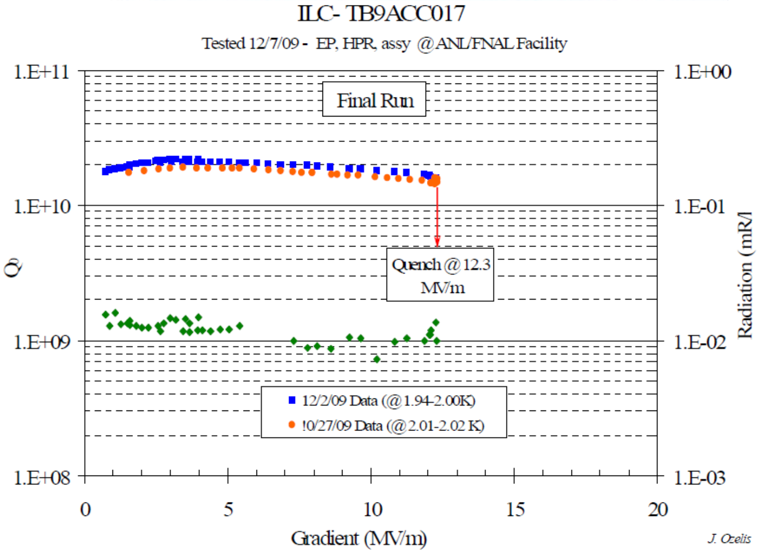
Cavity Surface Repair Laser re-melting technique

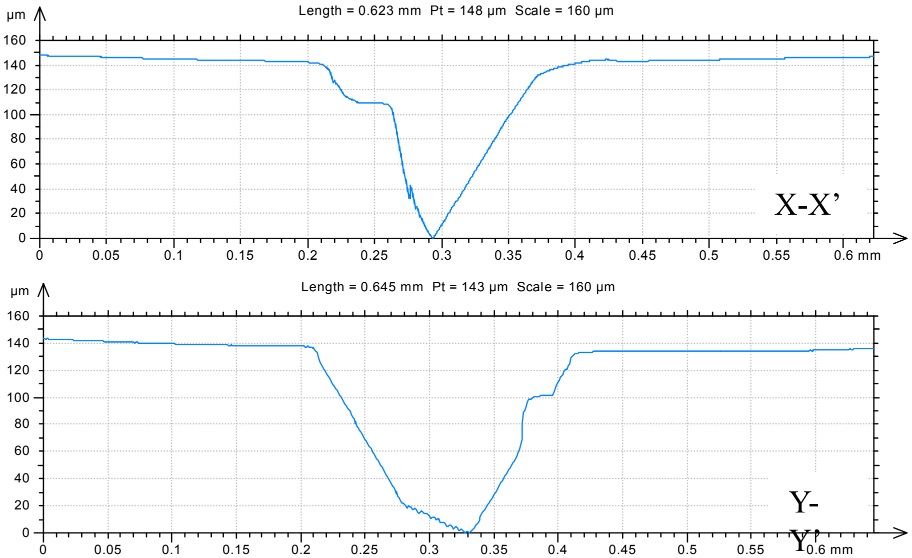
(M. Ge, et al. FNAL)

1.3GHz 9-cell cavity





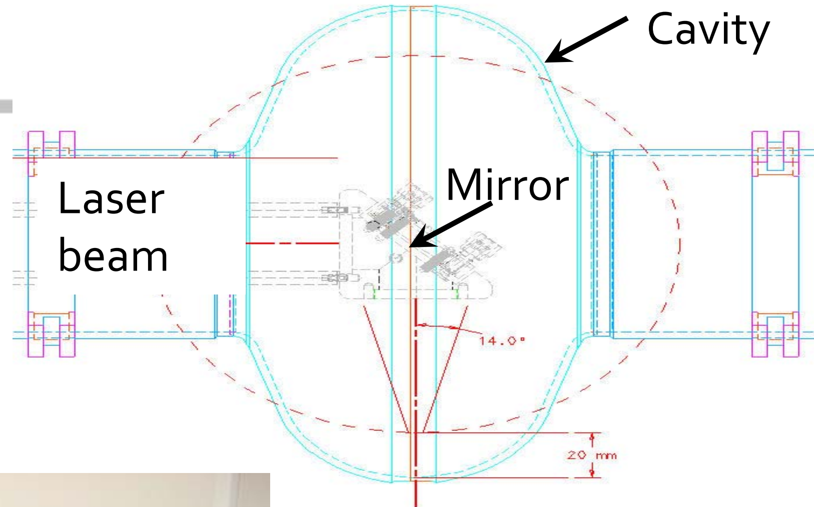


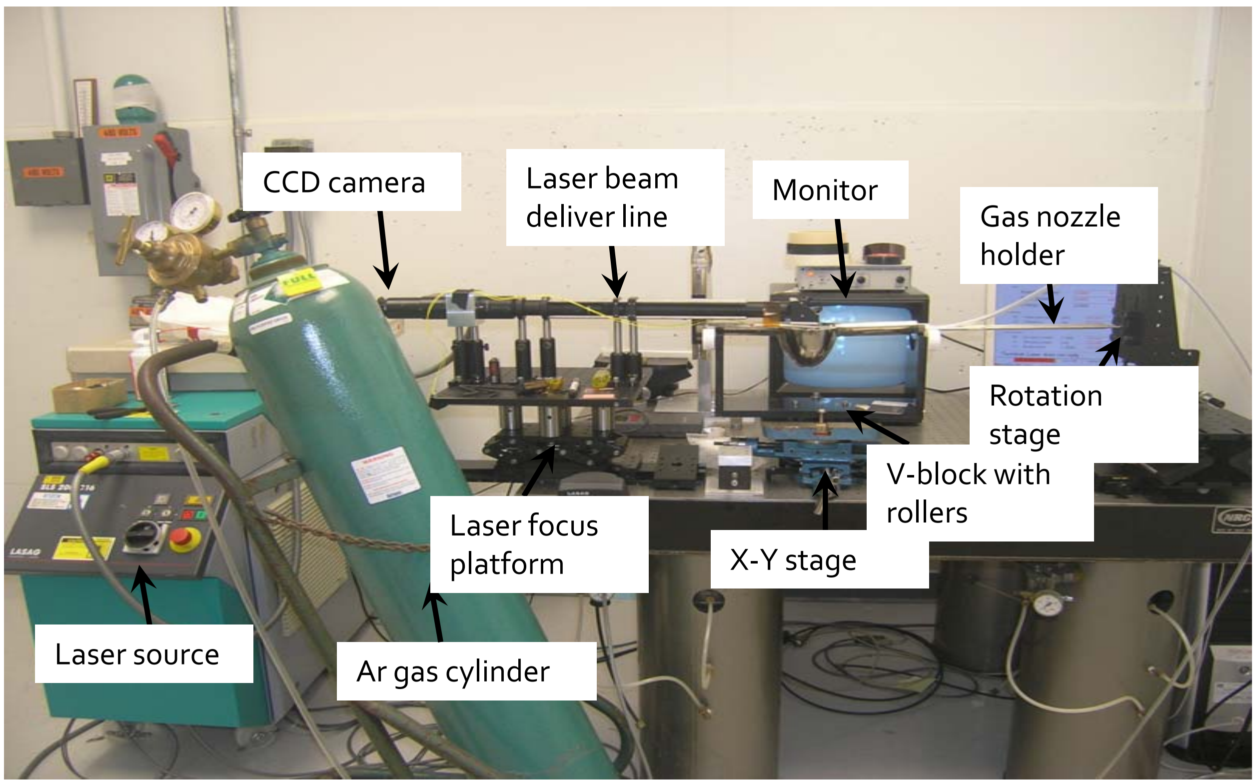


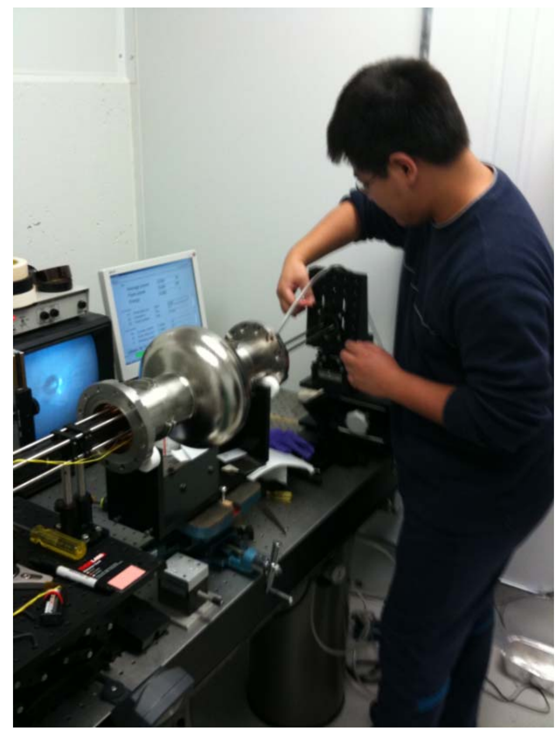
TB9ACC017 quenched at 12.3MV/m, Pit was found at Cell #4 equator 180 deg region (quench location), the pit is 150 µm deep and 200 µm wide on the top.

Laser repair tool

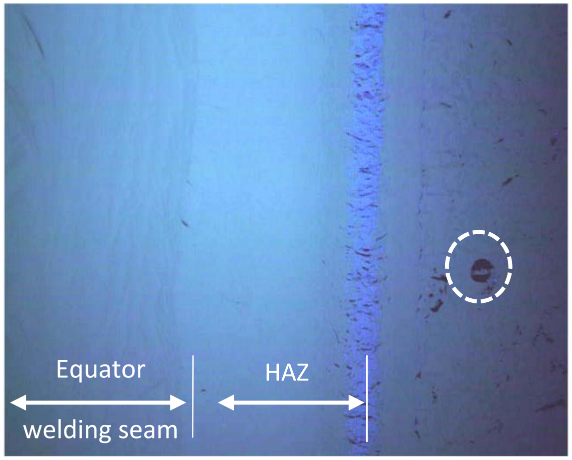
Goals:
Try to push cavity gradient from 20MV/m limited by pits to 40MV/m.



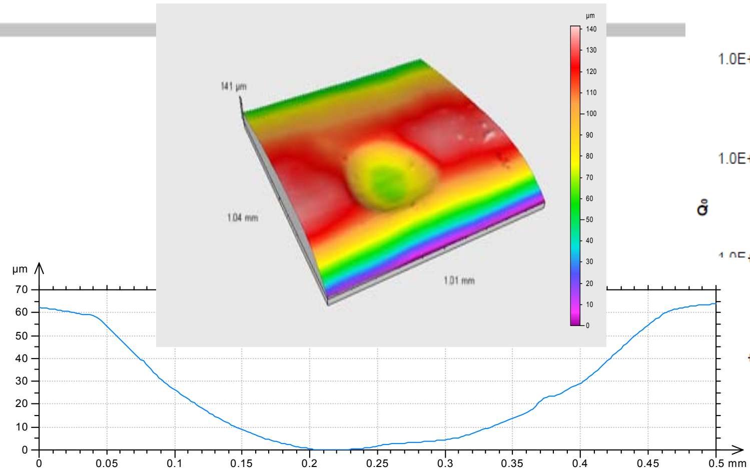




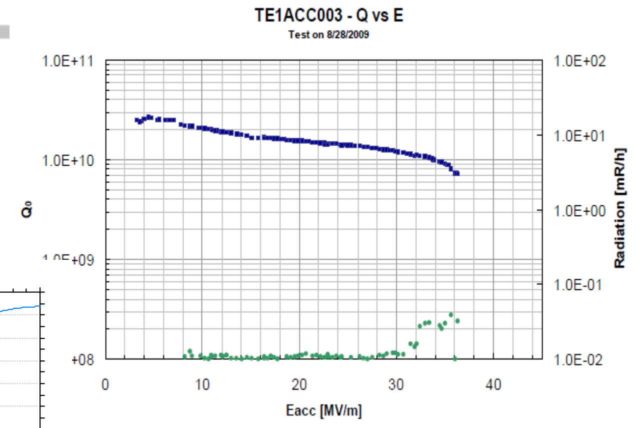
Experience from Fermilab 1.3GHz single-cell cavity activity



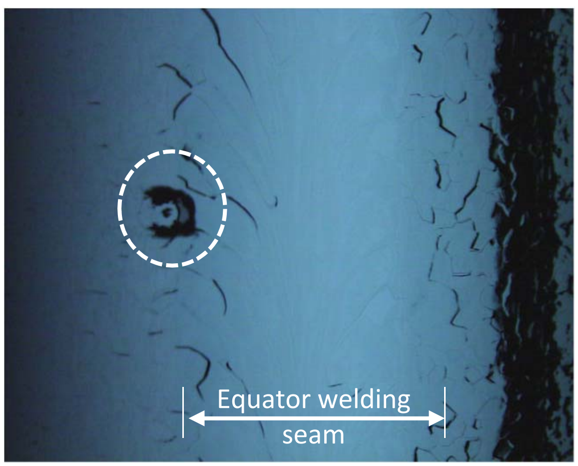
TE1ACC003



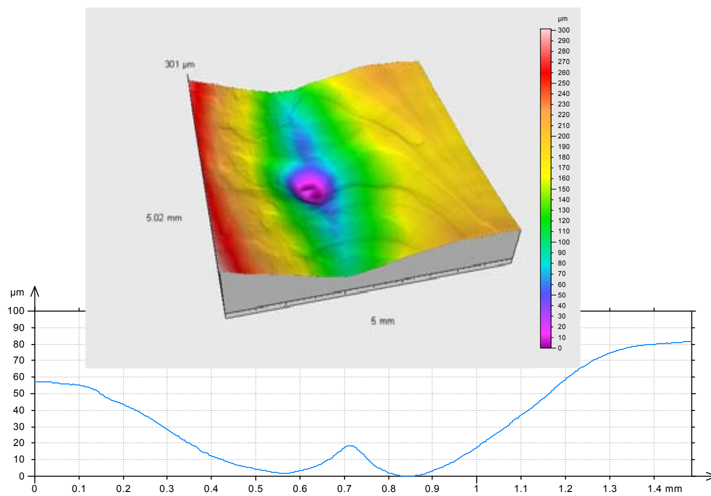
Diameter: 400µm,Depth: 60µm



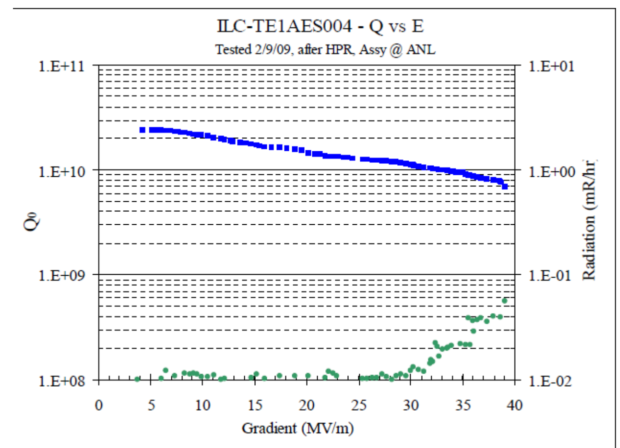
36MV/m quenched at pit region



TE1AES004

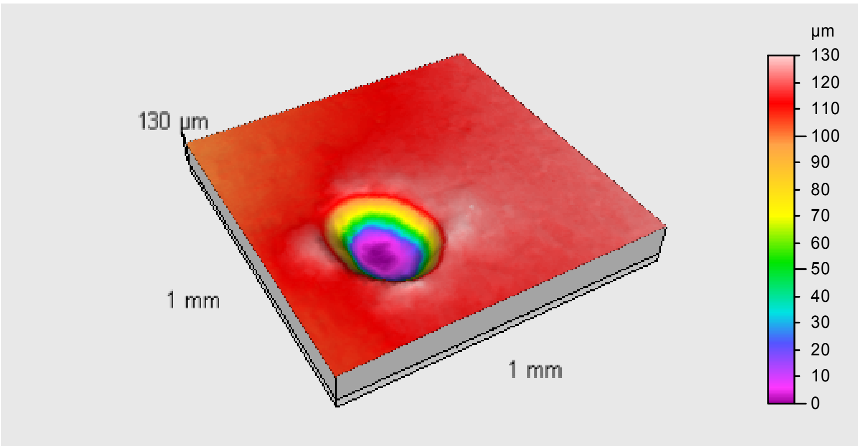


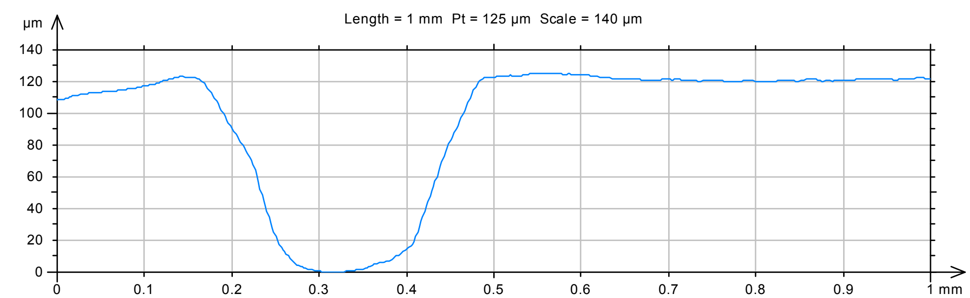
Diameter: 1300µm, Depth: 60µm
A 15µm tiny bump in the centre.



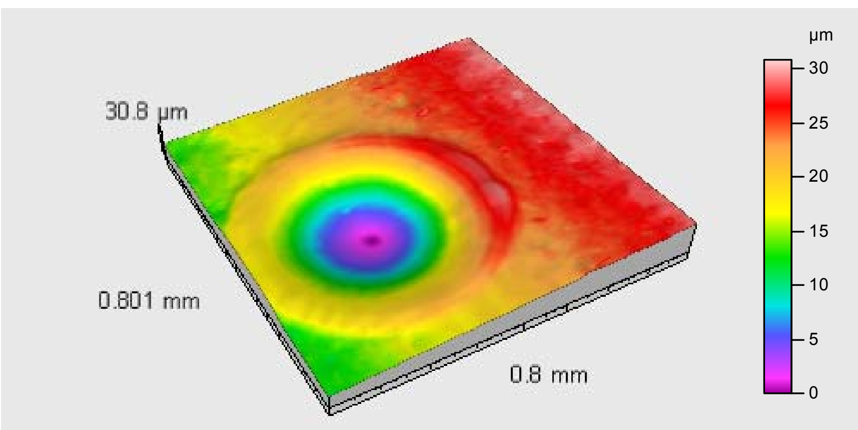
39MV/m quenched at pit region

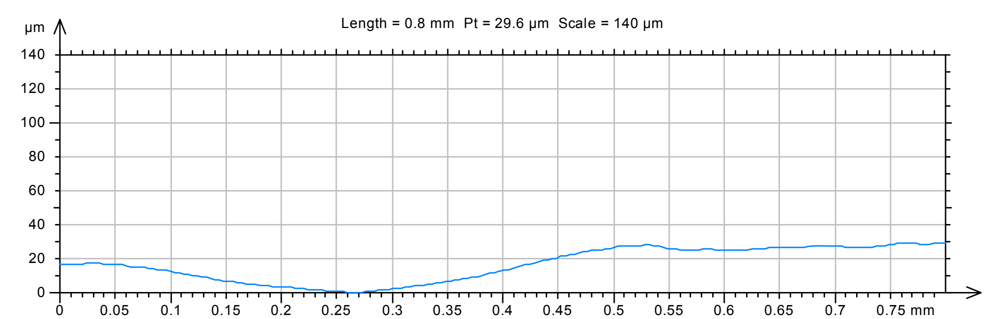
Profile Comparison before and after laser re-melting





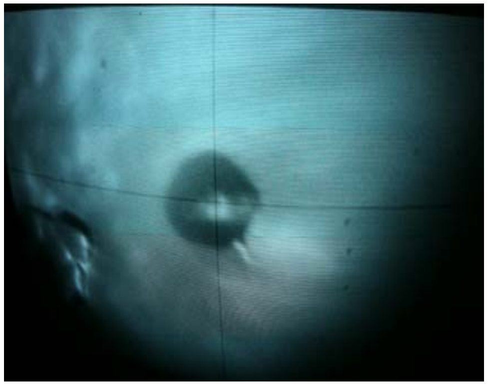
Manmade pit





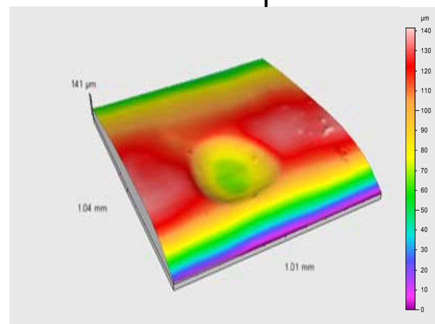
After re-melting the pit profile changed from 120µm deep to 30µm flat

Laser processing of 1.3GHz single-cell cavity (TE1ACC003)



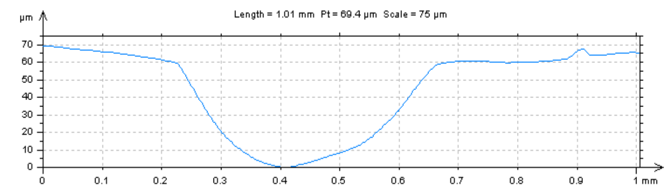
Screenshot of the monitor before and after laser re-melting

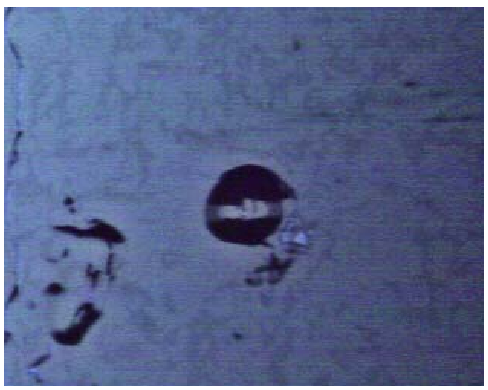
Profile comparison before and after Laser processing



400µm in diameter

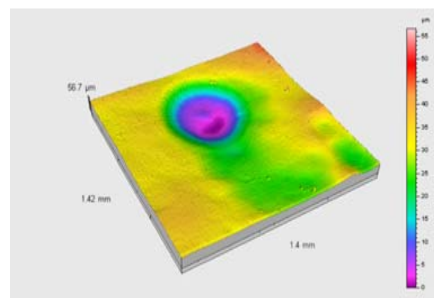
60 µm in depth





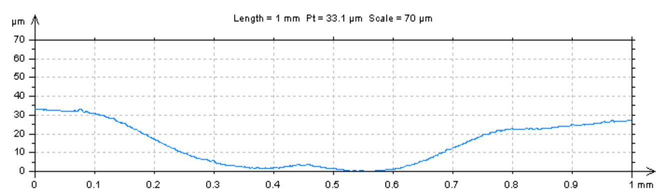
The Pit before re-melting

After re-melting



700µm in diameter

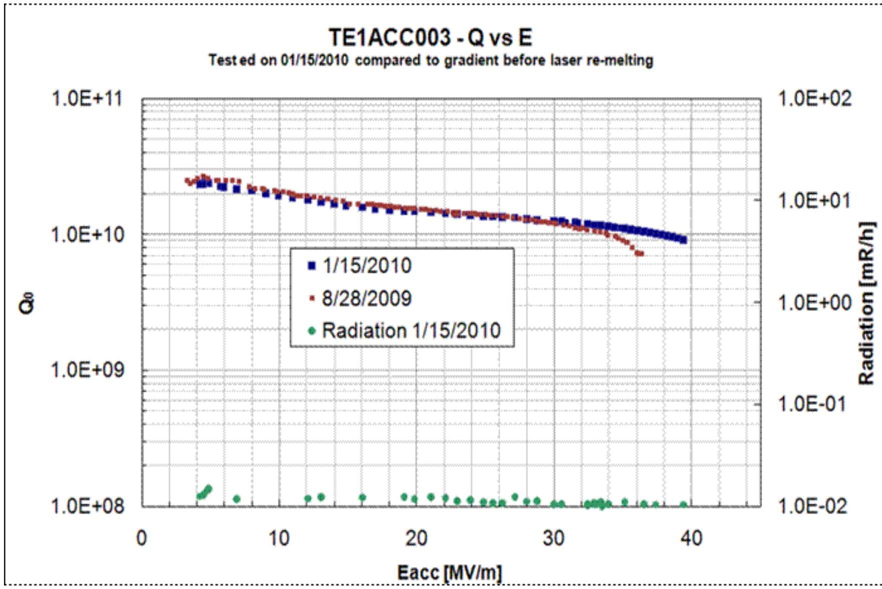
30 µm in depth

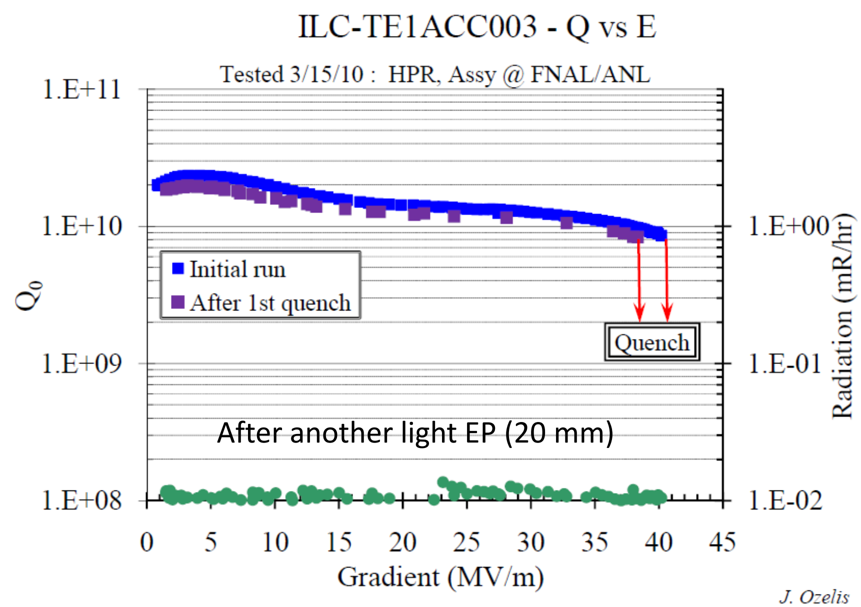


Images was taken from Kyoto Optical Inspection machine

The pit profile changed from 60µm deep to 30µm flat after re-melting and 50µm light EP

TE1ACC003 vertical test results before and after laser processing





After Laser processing: EP 20µm+HPR+120C baking;
Gradient achieved 39.4MV/m, quenched at molten region;
After flux trapped into cavity, cavity quenched at 32MV/m.

Cavity was EP'd another 30µm+HPR+120 °C baking;
Gradient achieved 40.3MV/m, quenched at molten region;
Cavity quenched at 38MV/m after first quench.

- Successfully re-melted pit inside 1.3GHz single-cell cavity.
- Cavity gradient achieved nearly 40MV/m.
- Flux trapping degraded gradient from 39MV/m to 32MV/m.
- Flux trapping was improved by additional EP (about 50µm).

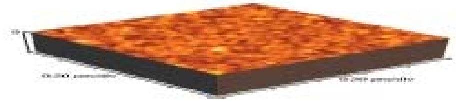
CAP LAYERS

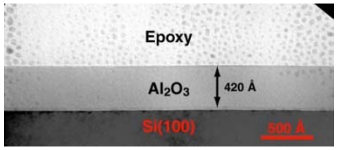
Atomic Layer Deposition (ALD)

T. Proslier, ANL.

Grow a dielectric oxide with superior properties to the Niobium Oxides

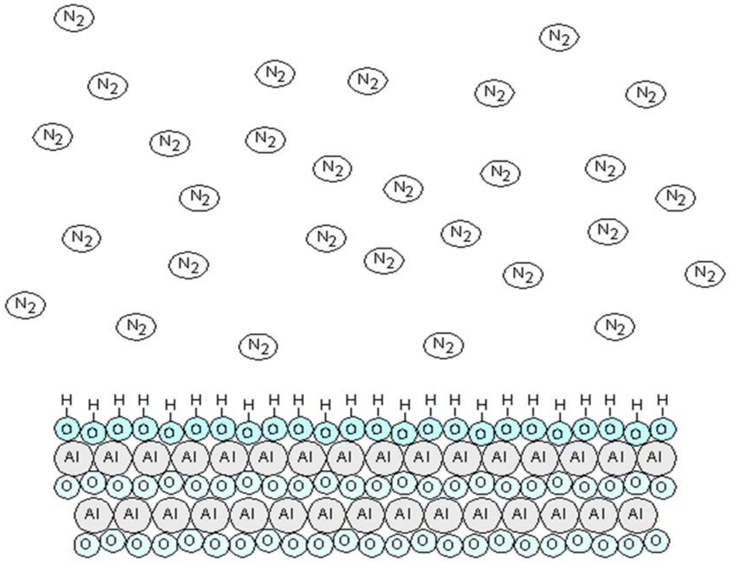
- Simple - non-interactive with the sc layer
- Passivating (stable surface, protective of the metal underneath)





ALD Reaction Scheme

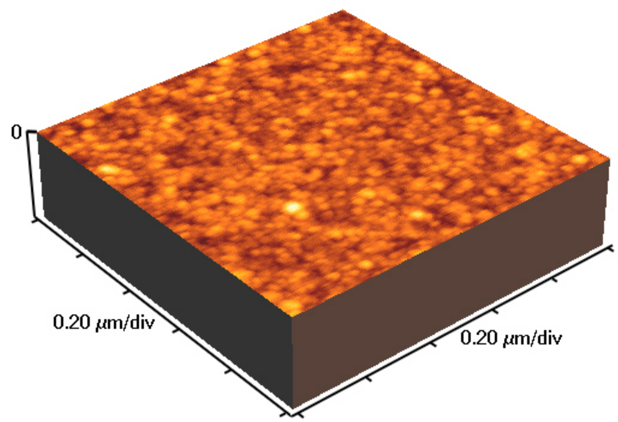
- ALD involves the use of a pair of reagents.
    - each reacts with the surface completely
    - each will not react with itself
- This setup eliminates line of site requirements
- Application of this AB Scheme
    - Reforms the surface
    - Adds precisely 1 monolayer
- Pulsed Valves allow atomic layer precision in growth
- Viscous flow (~1 Torr) allows rapid growth
    - ~1 mm / 1-4 hours



ALD Reaction Scheme

T. Proslier, ANL.

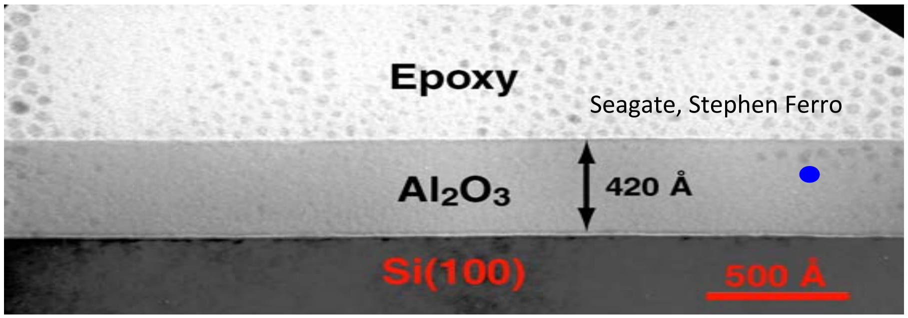
Atomic Force Microscopy



- RMS Roughness = 4 Å (3000 Cycles)
- ALD Films Flat, Pinhole free

Film growth is linear with AB Cycles

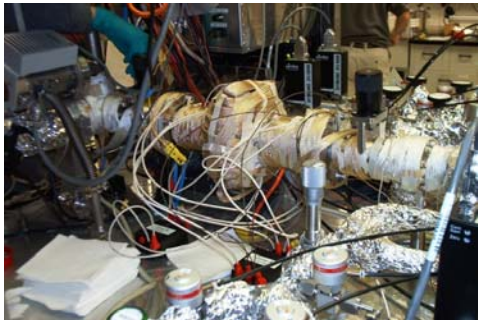
- **No uniform line of sight requirement**
- **Errors do not accumulate with film thickness.**
- **Fast (µm's in 1-3 hrs)**
- **Pinholes seem to be removed.**



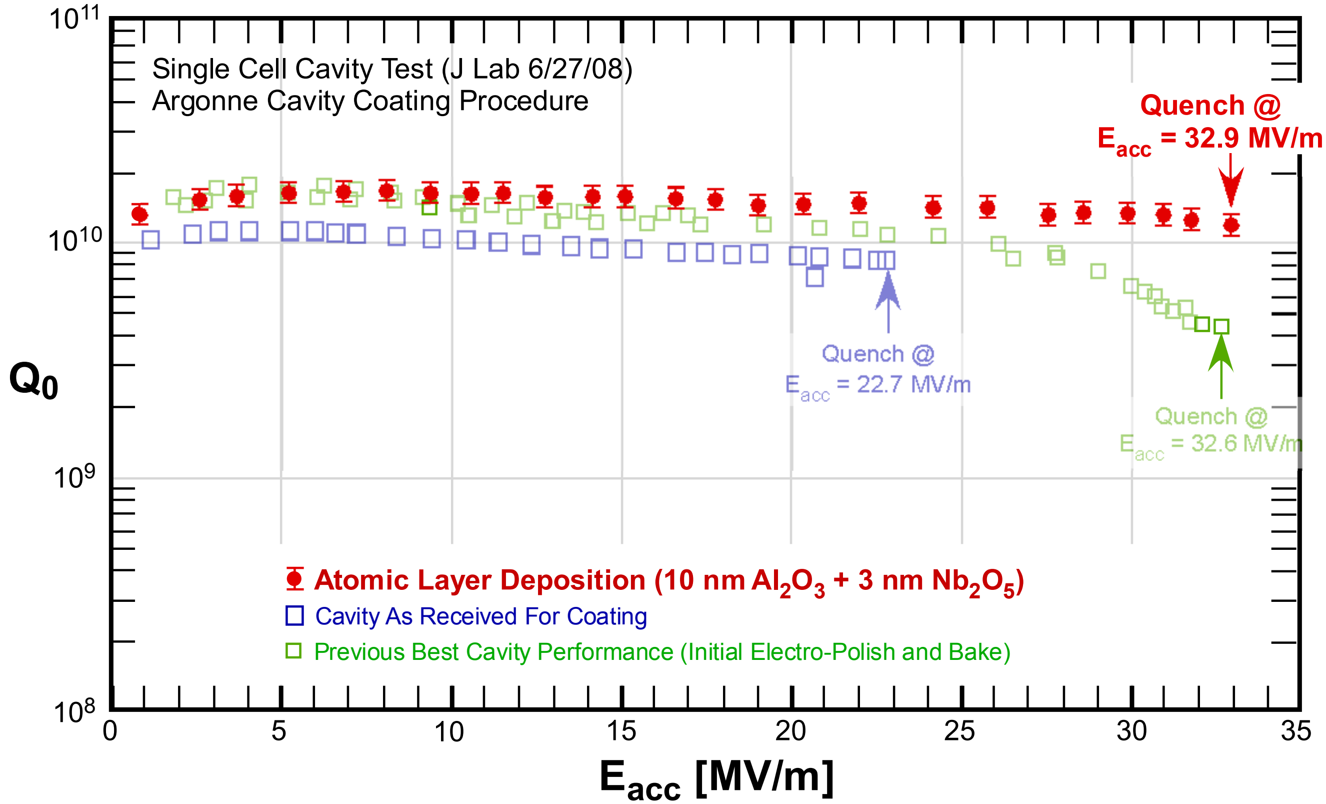
Flat, Pinhole-Free Film

JLab Cavity: After ALD Synthesis (10 nm Al_2O_3 + 3 nm Nb_2O_5)

T. Proslier, ANL.



1. Obtain a Single Cell Cavity from JLab
   a) "good" performance
   b) Tested several times
2. Coat cavity with 10 nm's Al_2O_3, 3 nm Nb_2O_5
   a) Niobia to reproduce original cavity surface
   b) Dust, clean room care
3. Acceleration Test at J Lab
   a) First test of ALD on cavities
   b) Check for "stuck" dust, high pressure rinse difficulties, material incompatibilities, etc.
   c) Goal: No performance loss
4. Bake @ Fermi, retest @ JLab (in progress)



- Only last point shows detectable field emission.
- 2nd test after 2nd high pressure rinse. (1st test showed field emission consistent with particulate contamination)

ALD - Conformal Coating Removes Field Induced Breakdown

T. Proslier, ANL.

- ALD is a compatible method for SCRF Cavity Processing.
- No significant multipacting.
  - Alumina underlayer does not enhance
  - Other surface choices? Many better choices than Nb_2O_5 are available.
- Field Emission reduction (dielectric improvement).
  - Alumina is a much better dielectric than Nb_2O_5
  - Is 10 nm optimum? Thicker, two step coating, etc.
- Improved Performance from last result.
  - 200 °C during layer synthesis + surface reduction
- Improved performance vs previous best
  - 3x improvement in Q, slight gradient enhancement
  - Anneal?

Normal conducting systems (*m*- cooling, CLIC) can also benefit.

- ~100 nm smooth coatings should eliminate breakdown sites in NCRF.
- Copper is a hard material to deposit, and it may be necessary to study other materials and alloys. Some R&D is required.
- The concept couldn't be simpler. Should work at all frequencies, can be *in-situ*.

- *In Situ* "ALD" Etching ($NbCl_5$ + 400 °C; 1 nm/cycle; Nb Metal)
  - Reduce or remove need to "dissolve" oxide
  - Controlled etching for C, O surface impurity control
  - Sub-oxide etching
- Multipacting, Emission Control (Nb_2O_5 used here)
  - What material?

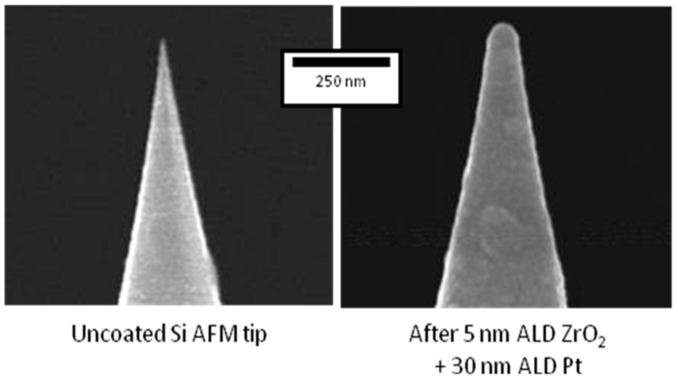


Figure 3: Scanning Electron Microscope images of nearly atomically-sharp tips, before and after coating with a total of 35nm of material by ALD. The tip, initially about 4 nm, has been rounded to 35nm radius of curvature by growth of an ALD film. Rough surfaces are inherently smoothed by the process of conformal coating.

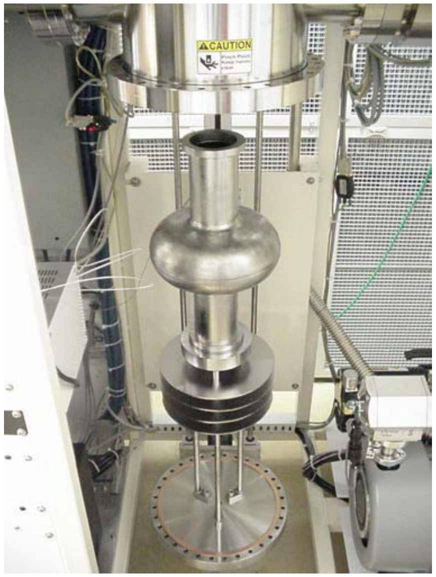
SURFACE DOPING (N, Ti)

CAVITY HEAT TREATMENTS OVER THE YEARS

- 1970s ~1800 °C UHV HT for ~10 hrs.
- 1980s ~1300 °C solid state getter, such as Titanium, was used in-side the furnace to "post-purify”.
- 2000s 600 °C 10h -800 °C 2-3h, mainly just to degas hydrogen absorbed by the Nb during cavity fabrication and surface treatments.
- 2010’s Clean furnace studies from 600 to 1400°C to reduce need for final chemistry
- 2012 “Doping” “polluting” “contaminating” cavity @ 800 to 1400 °C with titanium and Nitrogen – Extended Q-rise

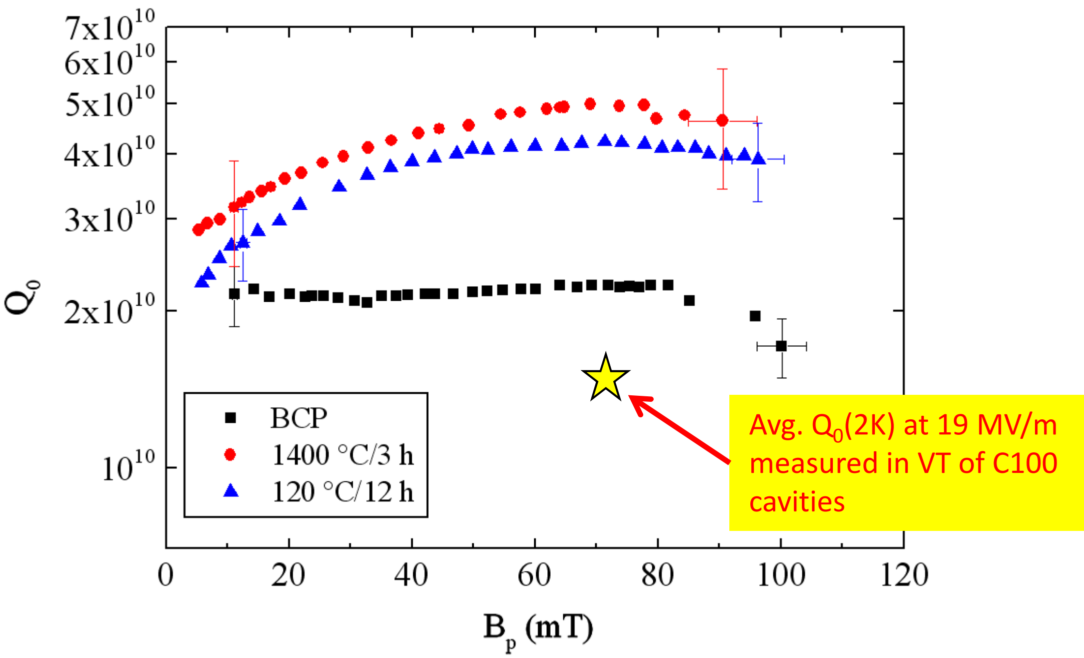
High-Q_o by Ti doping during furnace treatment

- A new induction furnace was designed and installed at JLab to continue the high-temperature annealing study above 800 ° C in a "clean" environment and without subsequent chemistry.
- In 2012, heat treatment at 1400° C/3h of an ingot Nb cavity with NbTi flanges at JLab resulted in doping of the surface with Ti (~1 at./%, ~1 mm deep) producing an unprecedented high Q0 $\cong 4.5 \times 10^{10}$ at 2 K, 90 mT



Samples analysis after 1400°C show:
- Reduced H content and ~1 at.% Ti content
- Higher energy gap and reduced broadening parameter

Ingot Nb cavity, 1.48 GHz, 2.0 K



P. Dhakal, Rev. Sci. Inst. **83**, 065105 (2012)
P. Dhakal et al., *Phys. Rev. ST Accel. Beams* **16**, 042001 (2013)
P. Dhakal et al., IPAC'14, p. 2651

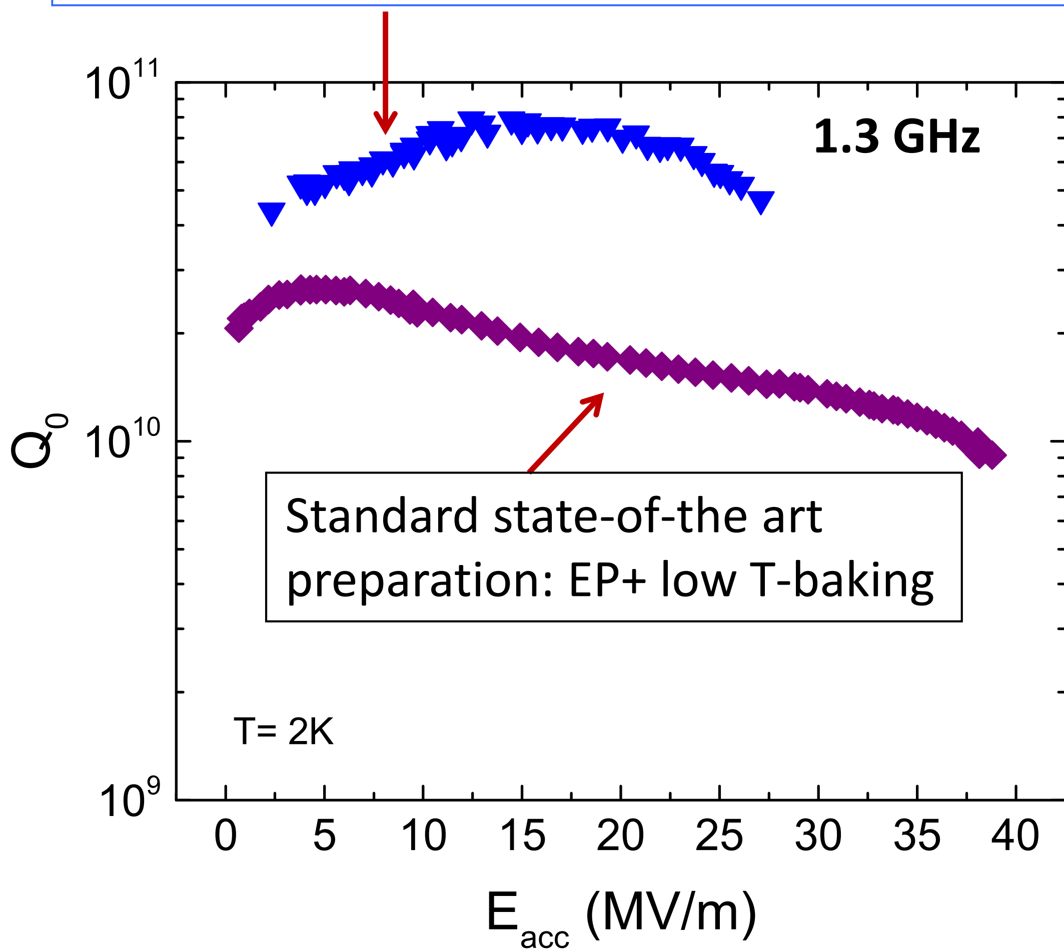
Nitrogen doping: a breakthrough in Q_0

- 2009 JLab attempted to make a Hydrogen blocking niobium nitride layer on the surface of a cavity (purposed in the 1970's), with no post heat treatment chemistry. Limited to $1e^{-4}$ torr because of interlock so higher pressures never used. ~30% gain in Q_0 (not doping).

G. Coivati et al., PRST - ACCELERATORS AND BEAMS 13, 022002 (2010)

- 2013 an attempt was made at FNAL to create niobium nitride (T_c=NbN) on the surface of the SRF cavity with nitrogen @ ~20mTorr and 800 °C. The experiment failed. Q = $1e^7$. But after random material removal ,cavity showed new Q-rise not seem before (except with Ti doping the year before) .

Record after nitrogen doping – up to 4 times higher Q!



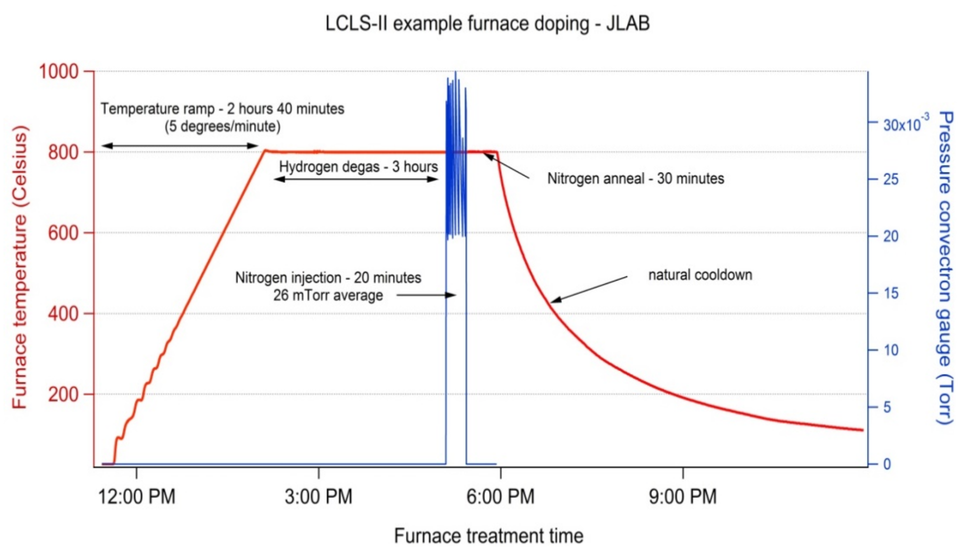
A. Grassellino et al, 2013 Supercond. Sci. Technol. **26** 102001

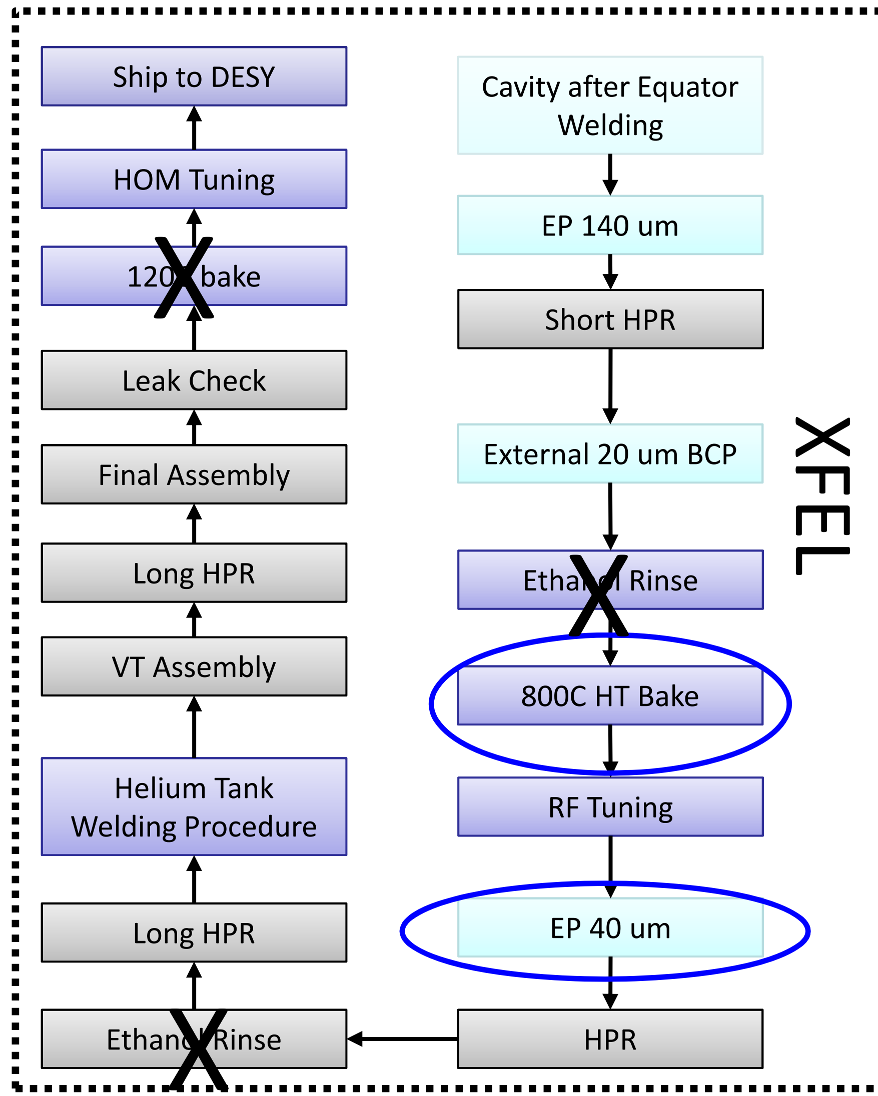
Doping treatment

small variation from standard XFEL/ILC processing recipe

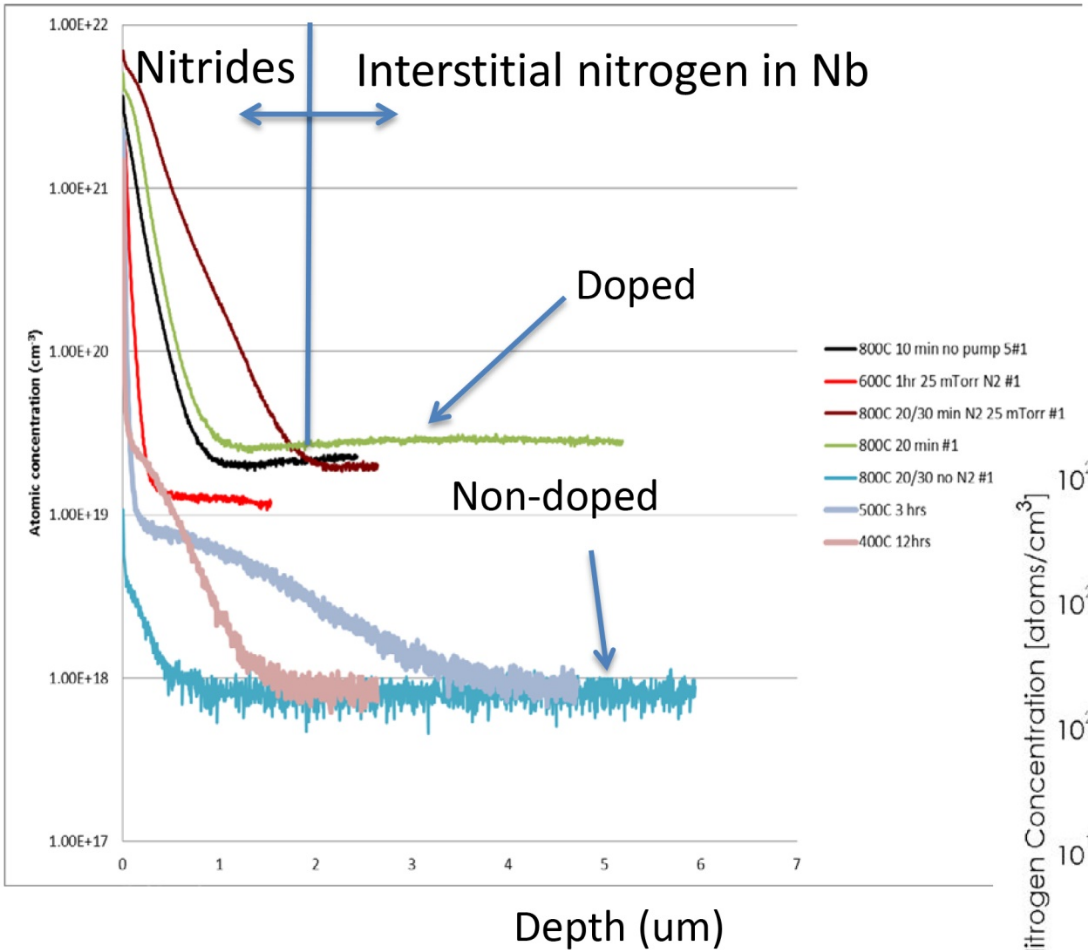
Example from N20/A30 doping process:

- Light BCP(internal) & Bulk EP (120)
- 800 ° C for 3 hours in vacuum
- Nitrogen @ 26 mTorr & 800 ° C (diffusion)
- 800 °C for 30 minutes in vacuum
- Vacuum cooling
- 16 µm EP

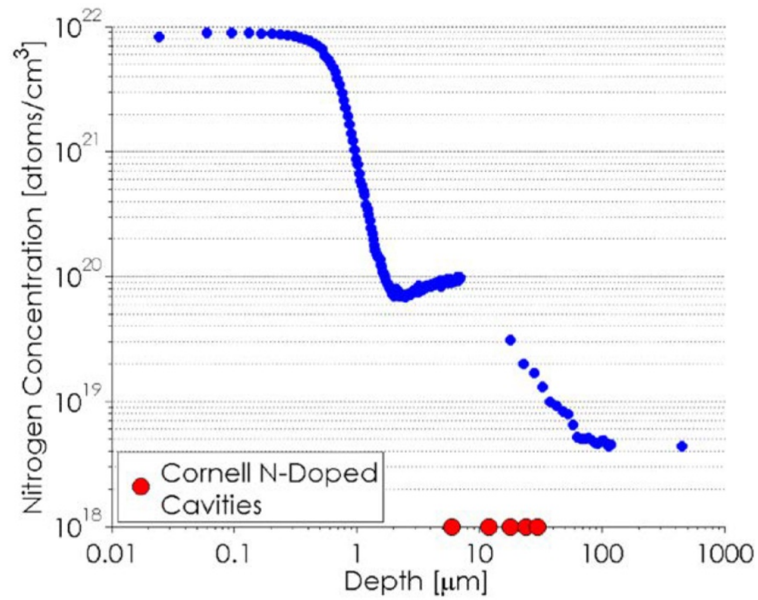




N surface doping : SIMS results

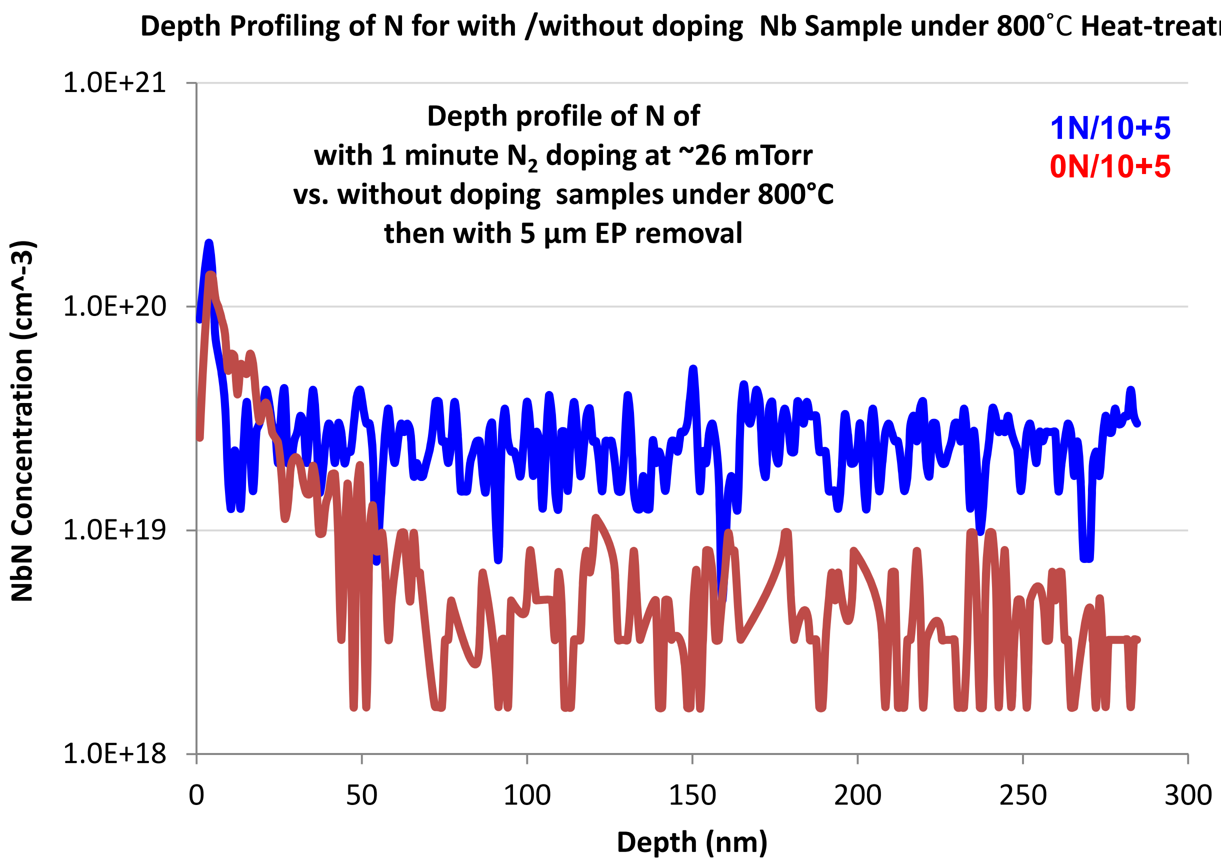


A. Romanenko, FNAL, LINAC 2014
D. Gonella, Cornell, LINAC 2014



N surface doping : SIMS results

N concentration drops to around 2~3×10^{19} level in less 1µm removal, and remains constant for up to 35 µm removal incrementally by EP for all measured N doped fine grain Nb samples (doping time, different annealing time). Nb samples having same heat-treatment without N doping show 3~5×10^{18} level of NbN (detection limit of TOF SIMS for NbN).

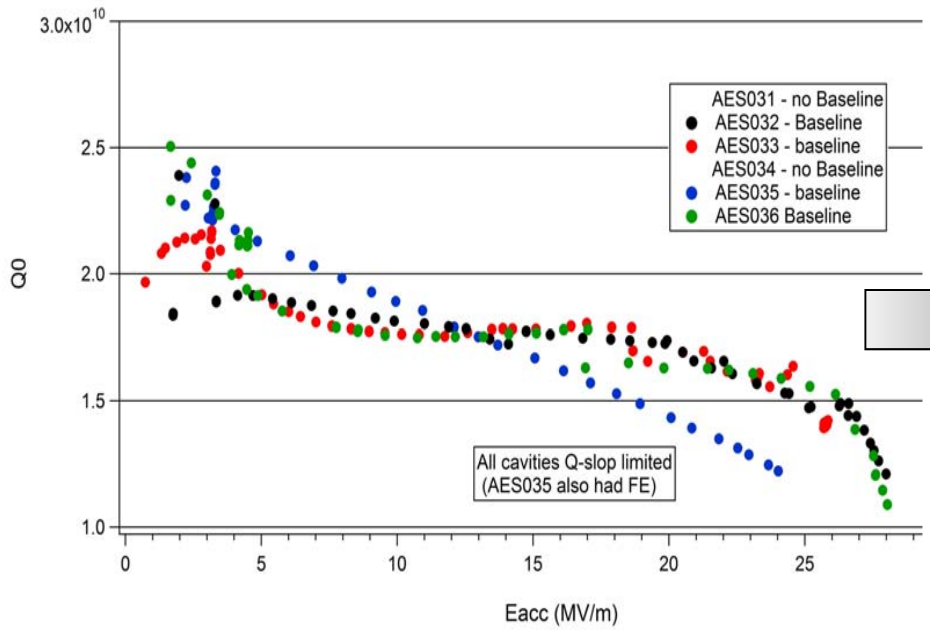


The short-hand notation **1N/10+5** denotes:

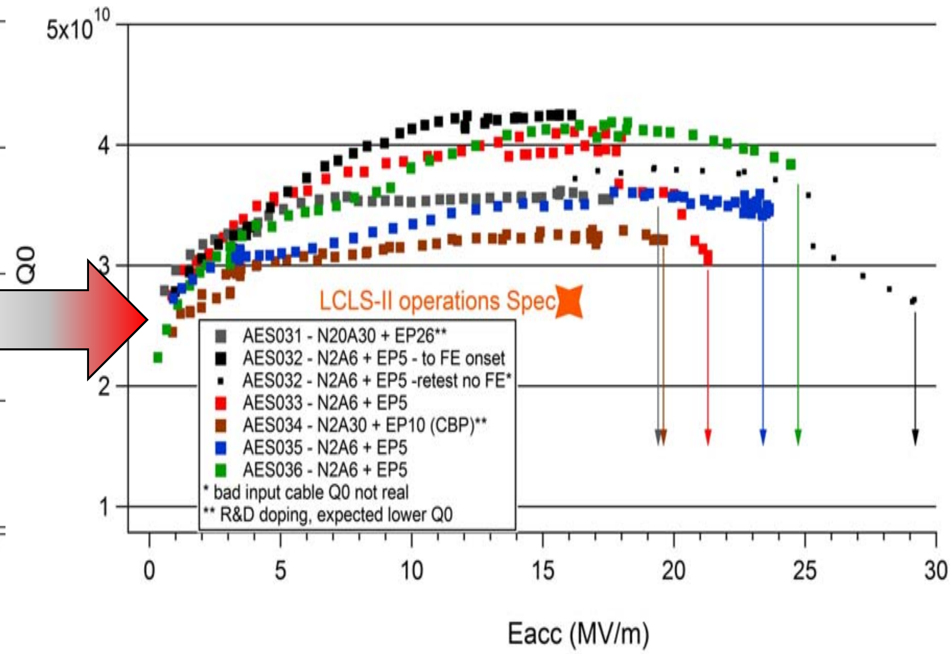
1. **1** minute exposure to ~ 26 mTorr N_2 @ 800 °C
2. **10** minute 800°C vacuum annealing
3. **5** µm electropolish

N surface doping : Improvements in Q

BASELINE RF TESTS AFTER BULK ELECTRO-POLISH



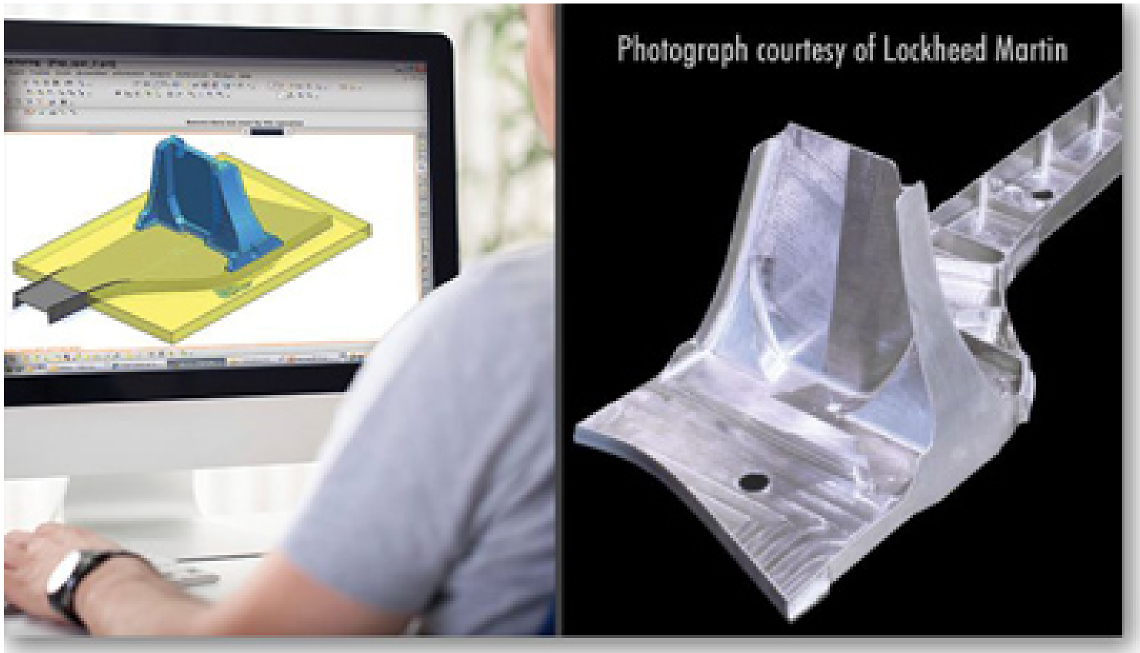
NITROGEN DOPING ROUND 2 RF RESULTS



All cavities were Q-slope limited, with AES035 also having some FE but not enough to limit the test

All cavities were tested with Stainless steel flanges which add 1.4 nΩ. Residual resistance with 1.4 nΩ has been subtracted from the data. –

Courtesy A. Palczewski JLab



ADDITIVE MANUFACTURING OF BULK NB

Bulk Nb Additive Manufacturing (3D Printing)

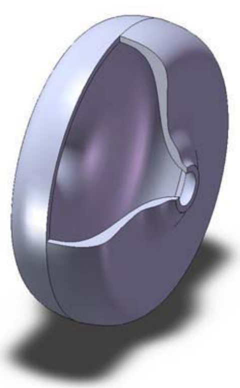
Electron Beam Additive Manufacturing (EBAM) Technology

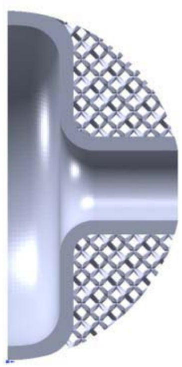
- ❑ Additive manufacturing techniques allow for higher average power and otherwise impossible designs
- ❑ Layers of atomized metal powder /wire is selectively melted with an electron beam

- ❑ An electron beam melts each layer to a geometry defined by a CAD model
- ❑ Fully-dense, functional parts
- ❑ Advantages: Cost/time savings
- ❑ Excellent material properties
- ❑ **Added freedom in design**

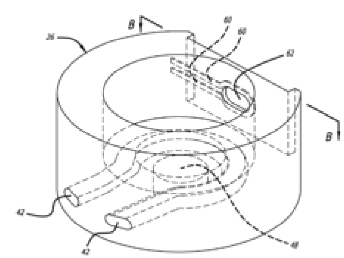
US Patent 7,411,361: *Method and apparatus for radio frequency cavity*;
Joint patent with JLab - pending: *Additive Manufacturing Method for SRF Components of Various Geometries*

United States
Patent Application Publication
AGUSTSSON et al.
Pub. No.: US 2008/0129203 A1
Pub. Date: Jun. 5, 2008





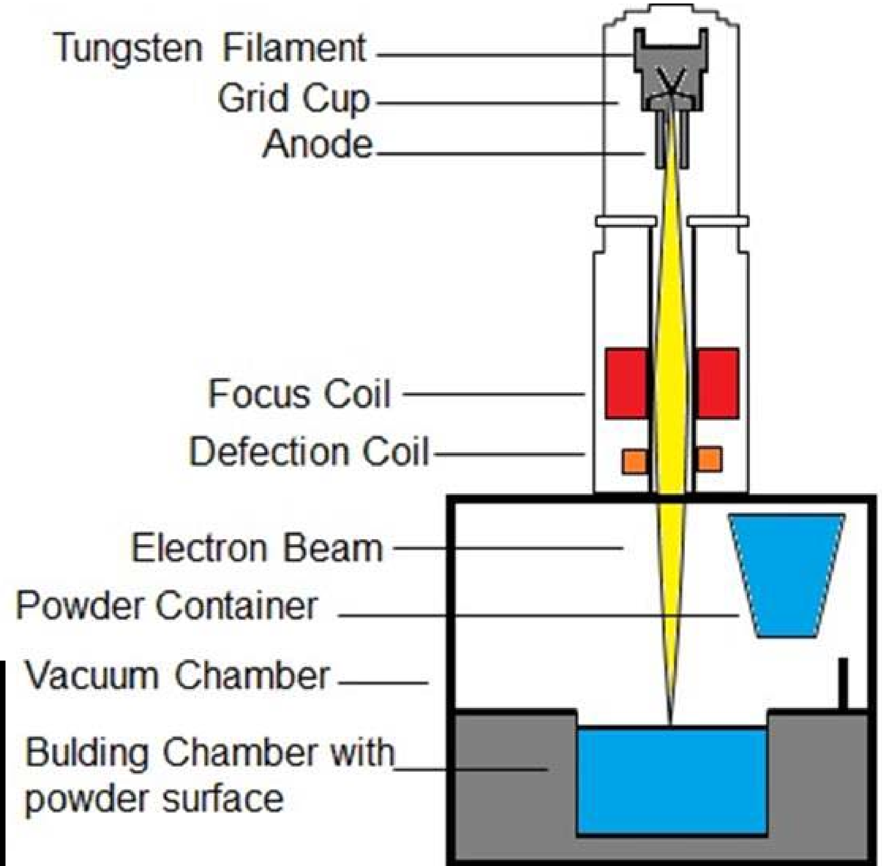
- ❑ Allows for nearly monolithic, seamless, and thermally-stabilized SRF niobium structures of arbitrary shape at reduced cost



Bulk Nb Additive Manufacturing

Electron Beam Melting (ARCAM)

- ❑ 4kW Electron beam is generated within the electron beam gun
- ❑ The tungsten filament is heated at extremely high temperatures which releases electrons
- ❑ Electrons accelerate with an electrical field and are focused by electromagnetic coils
- ❑ The electron beam melts each layer of metal powder to the desired geometry
- ❑ Vacuum/melt process eliminates impurities and yields high strength properties of the material
- ❑ Vacuum also facilitates the use of highly reactive metals
- ❑ High build temperature provides good form stability and low residual stress in the part
- ❑ 20-200 micron layer thickness
- ❑ 20-300 micron powder

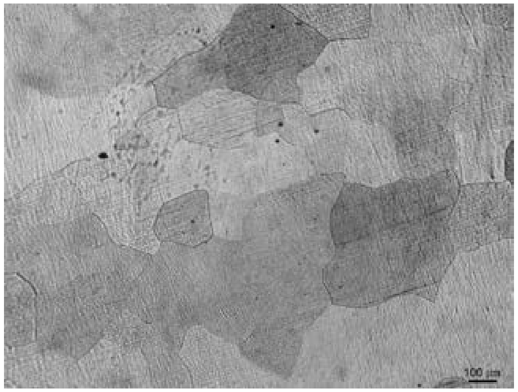


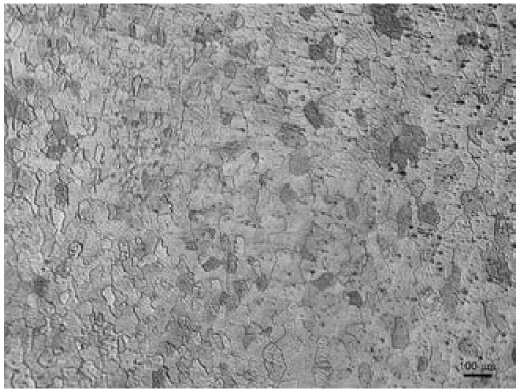
ARCAM A2 TECHNICAL DATA

Build tank volume	250x250x400 mm and 350x350x250 mm (W x D x H)
Maximum build size	200x200x350 mm and Ø 300x200 mm (W x D x H)
Model-to-Part accuracy, long range [1]	+/- 0.20 mm (3σ)
Model-to-Part accuracy, short range [1]	+/- 0.13 mm (3σ)
Surface finish (vertical & horizontal) [2]	Ra25/Ra35
Beam power	50–3500 W (continuously variable)
Beam spot size (FWHM)	0.2 mm – 1.0 mm (continuously variable)
EB scan speed	up to 8000 m/s
Build rate [2]	55/80 cm^3/h (Ti6Al4V)
No. of Beam spots	1–100
Vacuum base pressure	$<1 \times 10^{-4}$ mBar
Power supply	3 x 400 V, 32 A, 7 kW
Size and weight	1850 x 900 x 2200 mm (W x D x H), 1420 kg
Process computer CAD interface	PC
CAD interface	Standard: STL
Network	Ethernet 10/100/1000
Certification	CE

[1] Long range: 100 mm, Short range: 10 mm, measured on Arcam Standard Test Part (ASTP).
[2] Measured on Arcam Standard Test Part (ASTP).
Settings optimized for fine surface quality/Settings optimized for high build speed.

Bulk Nb Additive Manufacturing



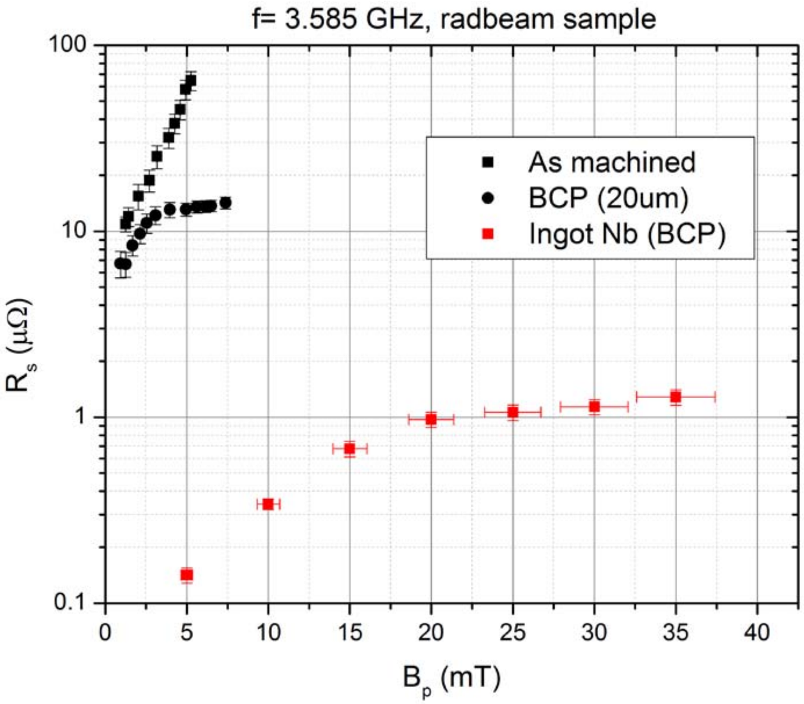


RRR measurements (4-probe method, JLab) show Uniform superconducting properties

T_c ~ 9.1 to 9.2 K, with sharp transitions

As-EBM, RRR ~ 17-18 (roughly half of feedstock material)

RRR ~ 44 after BCP dip +800˚ C 3hr HV in Ti box



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C. Terrazas t. al., *EBM Fabrication and Characterization of Reactor-Grade Niobium for Superconduc Applications*, Proceeding of Solid Freeform Fabrication Symposium, UT Austin, August 4-5, 2014

C. Terrazas, *Characterization of High-Purity Niobium Structures Fabricated using the Electron Beam Melting Prc* ,PhD Dissertation, UT El Paso, August, 2014

Concluding Remarks

- Non-exhaustive review of alternative processes for bulk Nb (
- Although Bulk Nb has been progressing for the past 40+ years and SRF performance is approaching the limit of Nb, there is some room for improvement as shown from the results of surface doping with N and Ti.
- With the advances in technology in other fields, manufacturing (additive manufacturing) and processing (ionic liquids, non-HF chemistry, plasma etching, ALD…) can be made cheaper, safer (personnel & environment) and more reliable.