Development of hydrofluoric acid-free EP treatment of Nb cavities at KEK

High energy accelerator research organization (KEK)

Takeyoshi Goto, Takayuki Saeki

Introduction: Importance of EP process in ILC project

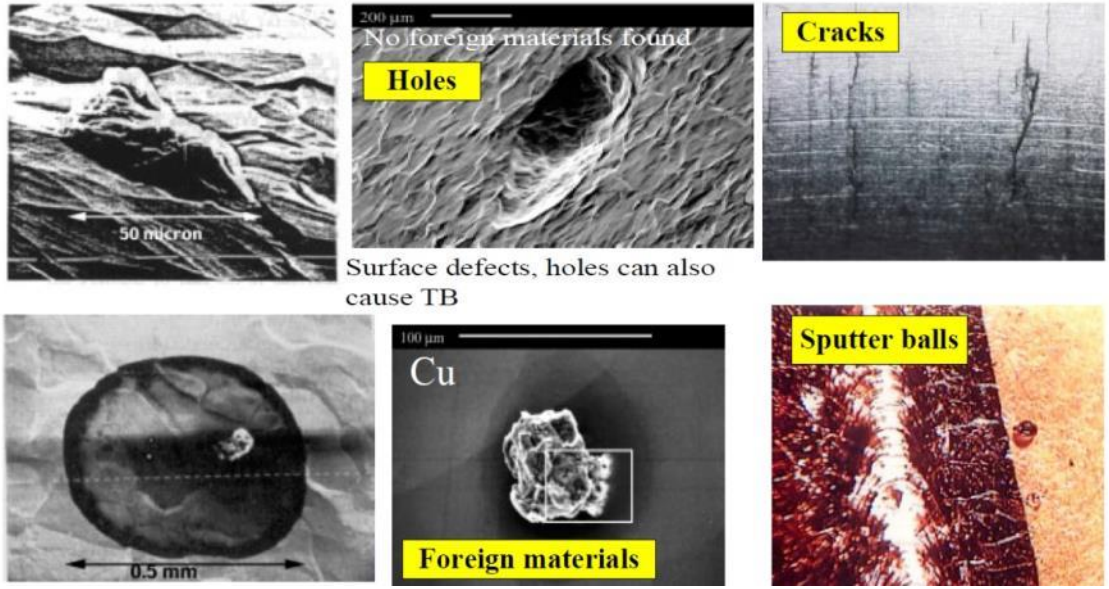
- The ILC project will require ~8000 9-cell Nb cavities.
- Electrolytic polishing (EP) treatment is essential for the high SRF performance of the cavities.

>> The surface of the Nb cavity after electron beam welding may have surface structures such as scratches and weld marks, so polishing process is required.

>> Mechanical polishing distorts the crystal structure of the Nb surface, so EP treatment is necessary to achieve a strain free surface.

- Dr. Saito (at KEK in ~1990) established a HF-EP method for Nb cavities using a mixture of hydrofluoric and sulfuric acids as the electrolyte.
- The HF-EP method was established as a protocol for the cavity treatment of ILC.

Surface defects and structures



Surface defects, holes can also cause TB

MP and EP

K. Saito, ILC-Asia-2004-03

HF-EP at KEK

- At KEK, the EP facility in the STF building has been performing HF-EP processing for more than 13 years without any major incidents.
- Currently, the installation of a vertical HF-EP facility is in progress in the COI building. (Commissioning to begin in 2022)

Anode: $2\,Nb + 5\,SO_4^{2-} + 5\,H_2O \rightarrow Nb_2O_5 + 10\,H^+ + 5\,SO_4^{2-} + 10\,e^-$

Cathode: $2\,H^+ + 2\,e^- \rightarrow H_2$

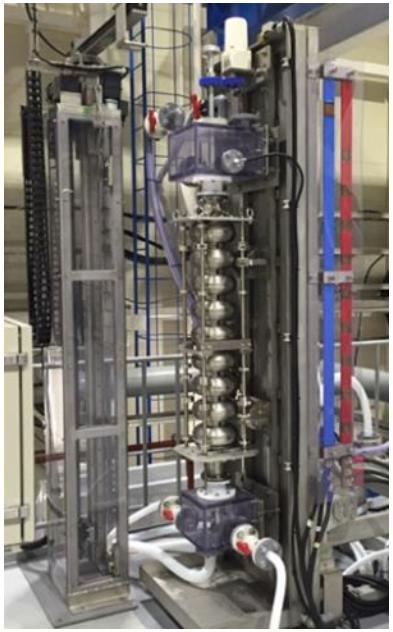
net reaction: $\boxed{2\,Nb + 5\,H_2O \rightarrow 5\,H_2 + Nb_2O_5}$

dissolved as Nb fluoride salts

Dissolution of Nb oxide: $Nb_2O_5 + 12F^- + 10H^+ \rightarrow 2NbF_6^- + 5H_2O$

horizontal EP at STF

vertical EP at COI



Very high cost of HF-EP process

Electrolyte of HF-EP: HF(48wt%) : H_2SO_4 (98wt%) = 1 : 9 (v/v)

- Strict measures must be taken for chemical safety and prevention of the electrolyte leakage to the environments. (strict regulations, special equipment, training of workers..)

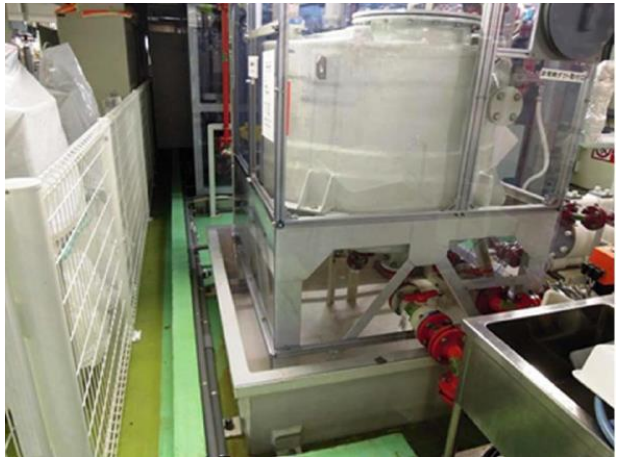
>> HF-EP facilities are very complex and special.
acid-resistant parts, complex piping, many interlock systems...

>> Disposal of a large amount of liquid waste containing fluoride.

- The construction of HF-EP facilities is very expensive. There are few companies in the world that can build new HF-EP facilities just for the ILC project.

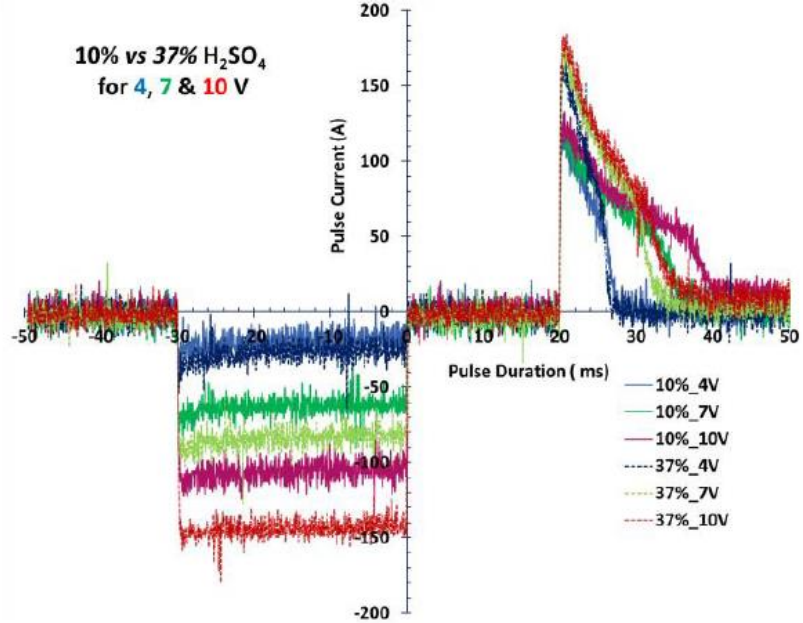
>> The HF-EP process accounts for a very large fraction of cost of ILC project.

>> We have been developing bipolar- and AC-EP as HF-free EP methods.

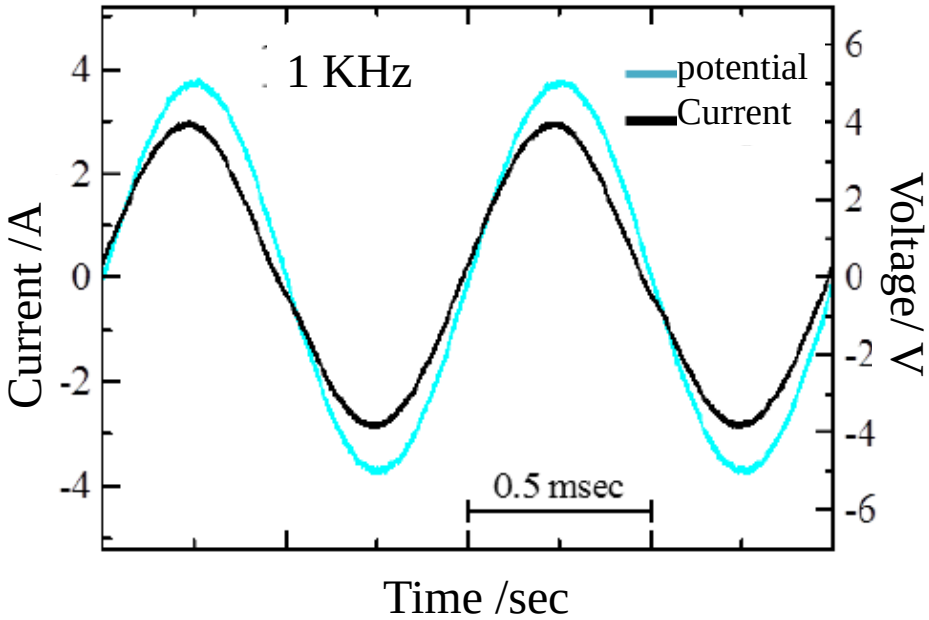


HF-free EP methods: bipolar and AC

Bipolar millisec pulse current



AC: ~KHz



Tian, H.; et al. *Proc. 29th Linear Accel. Conf. LINAC 2018* **2020**, 431.

Kawamura, Master Thesis, **2015**, Iwate University

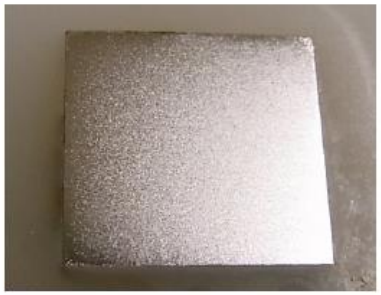
- Aqueous electrolyte without HF. (10~35wt% sulfuric acid aqueous solution)
- high millisec pulse current or highly repetitive current (KHz).
- Anodic current to oxidize Nb surface, then physicochemically erode the Nb oxide layer by repeated H_2 formation (cavitation, reduction of Nb, and more..?).

BP-EP method (1) KEK and Nomura Plating Co.

- Umehara, M.; et al. Proc. LINAC14, **2014**, 1102.
- Taguchi, J.; et al. *IPAC 2016 - Proc. 7th Int. Part. Accel. Conf.* **2016**, No. 1, 2020.
- Taguchi, J.; et al. *18th Int. Conf. RF Supercond.* **2017**, 623.

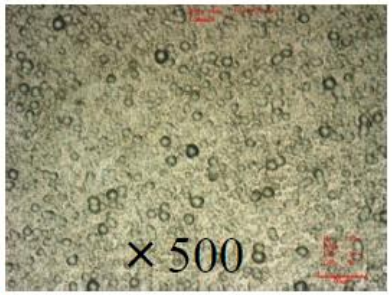
Before EP, Ry = 2.3 μm

H_2SO_4



Surface roughness

Ry=2.1 μm

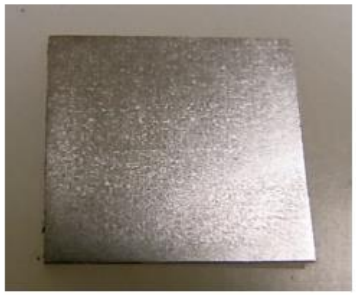


T= 20°C
Conc.
10% H_2SO_4

T_{anodic}	10 ms	I_{anodic}	+0.6 A
$T_{cathodic}$	2 ms	$I_{cathodic}$	-2.4 A

some black dots left

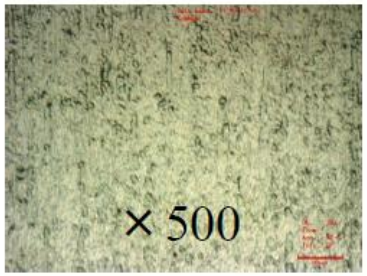
NaOH



Surface roughness

Ry=1.5 μm

Polishing time = 30 min



T= 50°C
Conc.
10% NaOH

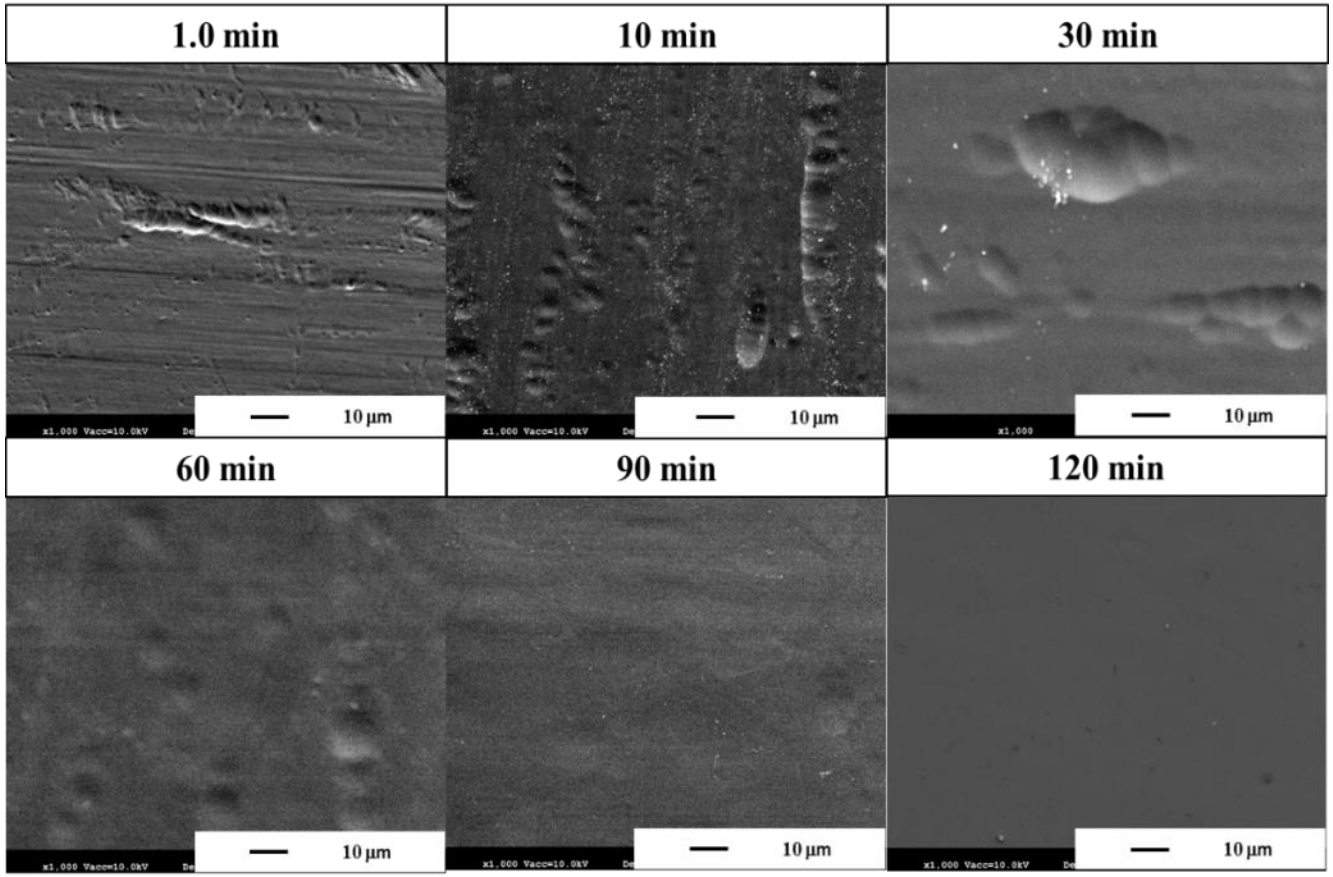
Patented

T_{anodic}	10 ms	I_{anodic}	+0.6 A
$T_{cathodic}$	2 ms	$I_{cathodic}$	-2.4 A

BP-EP method (2) Iwate University, KEK, and Marui Plating Co.

Miura, Y; et al. 67th Zairyou to Kankyou touronnkai, October, 2020.

25°C, 30wt% H_2SO_4, *anode:* +10 V, 2 ms, *cathode:* −3 V, 2 ms.



- It took 60 min to attain the flab Nb surface at optimal condition (anode pulse time: 1 ms).

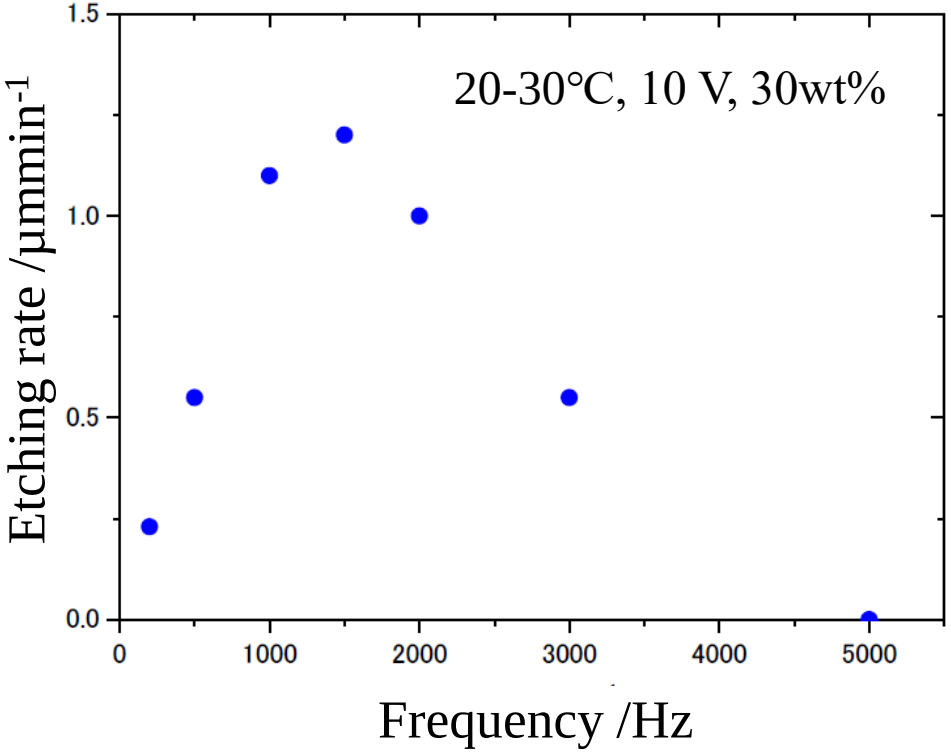
>> In order to obtain a flat surface by BP-EP, it is necessary to remove a large amount of Nb.

AC-EP method

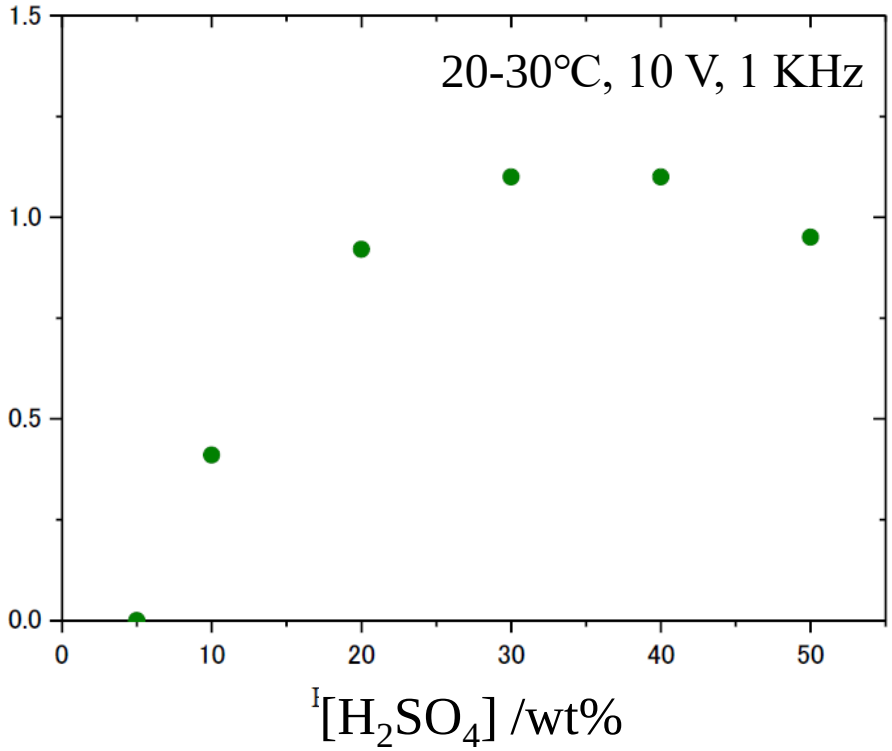
Iwate University, KEK, and Marui Plating Co.

Kawamura, Master Thesis, **2015**, Iwate University

Frequency



$[H_2SO_4]$



- Optimal condition of etching rate: 20-30°C, 10 V, 30wt% H_2SO_4, 1 KHz.
- The polishing condition for a sufficiently flat surface of Nb has not been found yet.

Are BP- and AC-EP methods applicable to 9-cell cavities?

BP- and AC-EP methods are difficult to process the whole ~8000 9-cell Nb cavities.

1) The energy efficiency of polishing in BP- and AC-EP is very low.

- Those require very high capacity programmable power supply systems, which are very spacious, complex, and high cost.
- Those produce large waste heat.

2) Since BP- and AC-EP methods are not only chemical polishing but also physical polishing, the surface variation may be larger for samples with large surface area.

- The rate-limiting factor for HF-EP is the HF concentration, and it is easy to make the diffused HF concentration distribution uniform on the entire 9 cell cavity surface.
- For BP- and AC-EP, the dissolution of the oxide film is caused by the H_2 gas formation (cavitation, reduction of Nb..?), and the dissolution rate tends to be uneven.

3) For BP-EP, at least a few tens of microns need to be eroded to attain surface flatness.

4) 10~35wt% H_2SO_4 aqueous solutions are not chemically safe enough.

Recently, we have started to study new HF-free EP methods.

1) DC-EP: a) salts in ethylene glycol-ethanol and b) alkali aqueous solution with ethanol

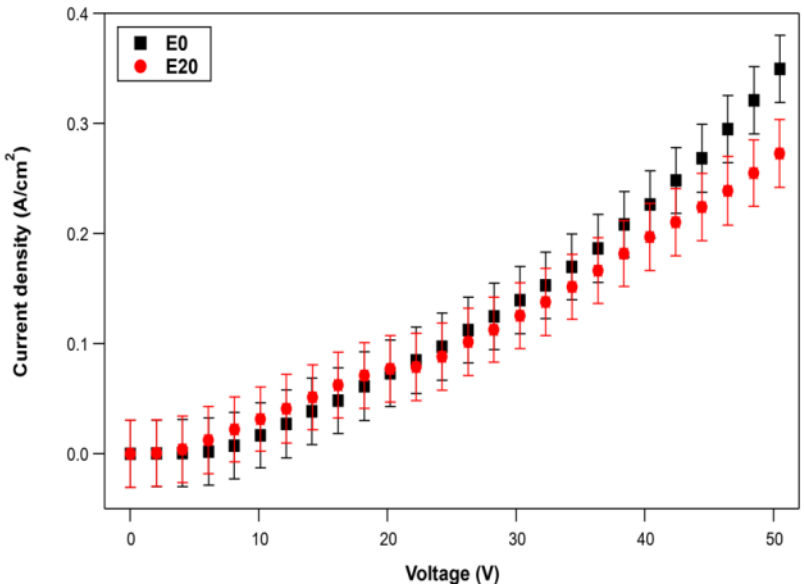
2) Jet Plasma EP for local polishing of Nb cavities.

DC-EP: NaCl in ethylene glycol + additives

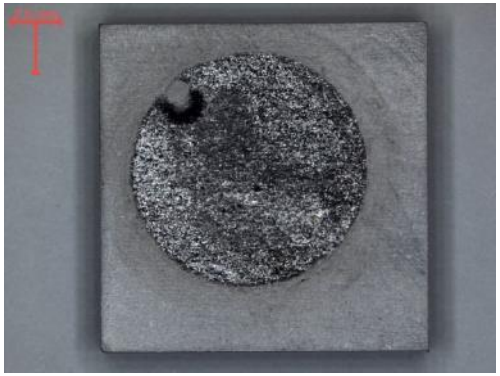
Dr. H. Takechi (KEK)

Anode: Nb (1 cm^2), Cathode: SUS304, Temp.: 20°C
Electrolyte: 1 M NaCl in ethylene glycol + ethanol 20% v/v

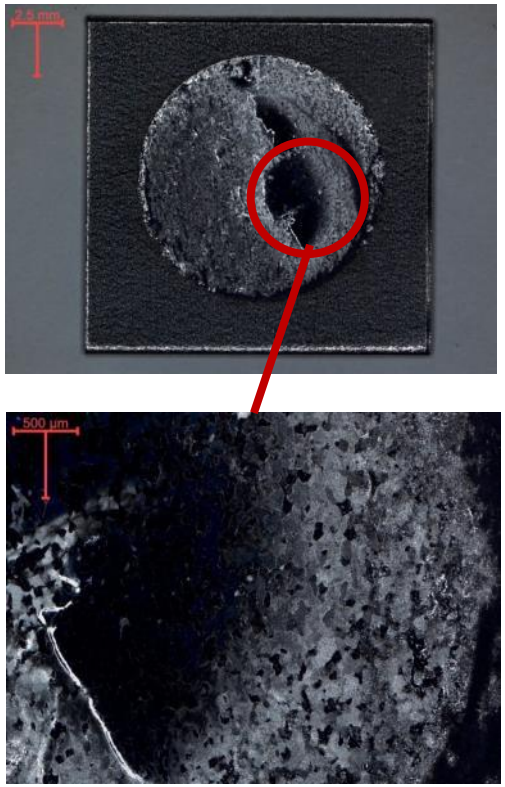
Polarization curve



E0, 20 V, 50 min
etching: 16.2 mg



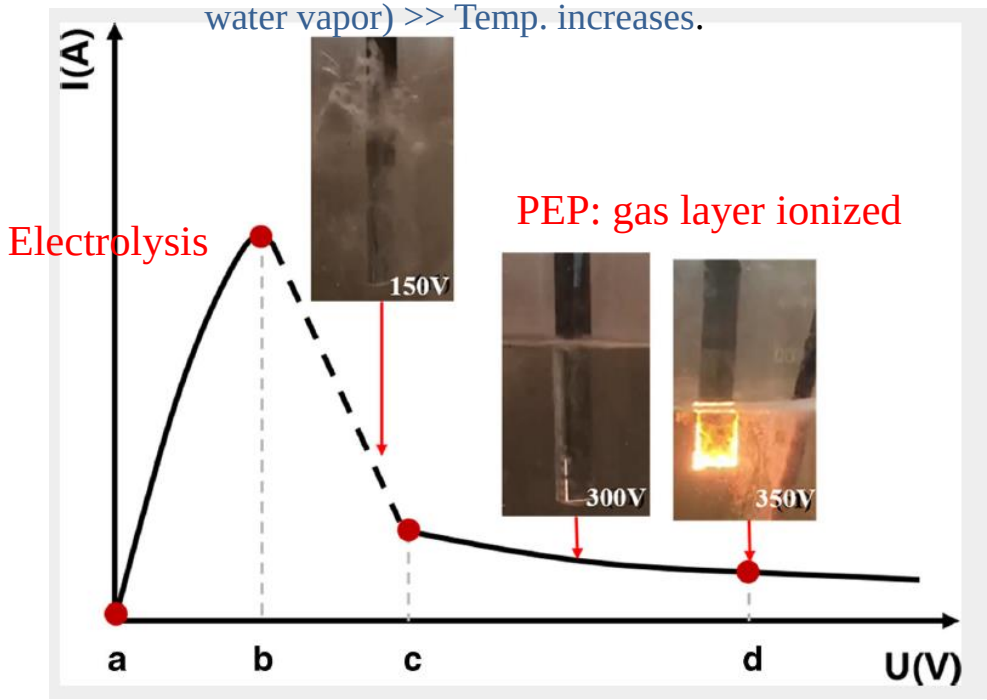
E20, 20 V, 50 min
etching: 24.6 mg



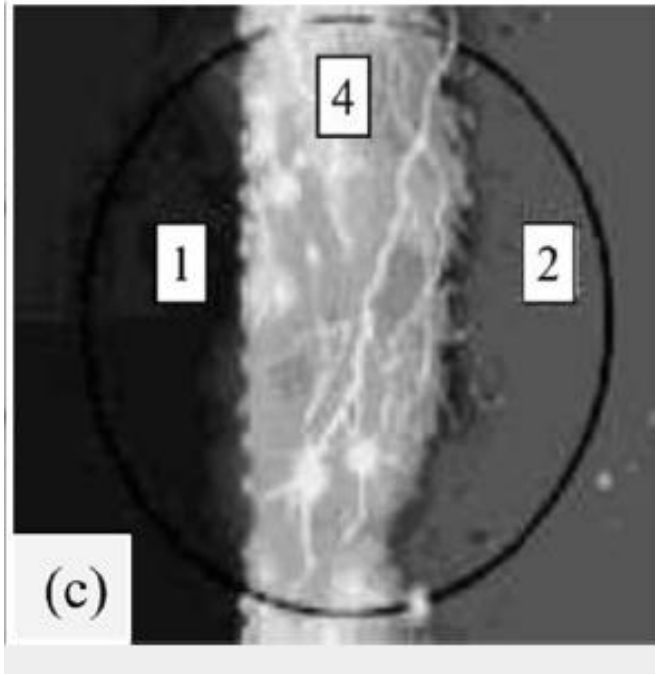
- Nb plate was electrolyzed.
- It was partially well polished with the addition of EtOH.
- Vertical streak on the surface.
  >> The viscos layer was dripping by gravity.
- The optimal conditions resulting in the entire mirror-like surface are still being investigated.

Other HF-EP alternative method: Plasma electrolytic polishing (PEP)

Insulating gas layer (mostly water vapor) >> Temp. increases.

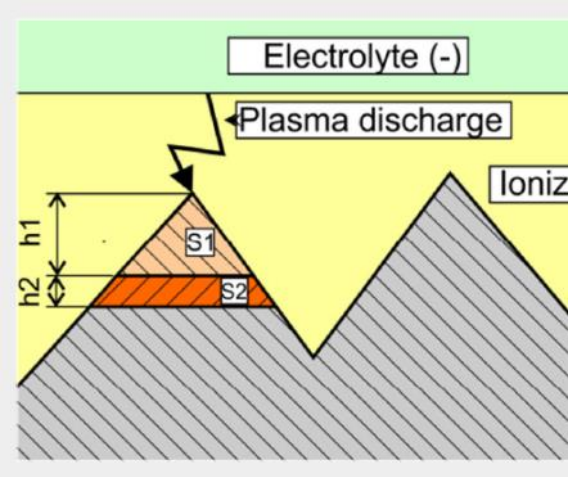


Huang, Y.; et al. *Int. J. Adv. Manuf. Technol.* **2021**, *114* (7–8), 1893.



- Surface material removal mostly by local gas explosion caused by gas expansion and magnetic confinement in discharge channel.
- Operation DC condition: ~300 V, ~0.5 A/cm^2
- Electrolytes: a few % of salt aqueous solutions (typically, ammonium sulfate and chloride)
- Very smooth polished surface (Ra less than 0.1 μm)
- Very fast etching rate (more than 10 time faster than HF-EP)

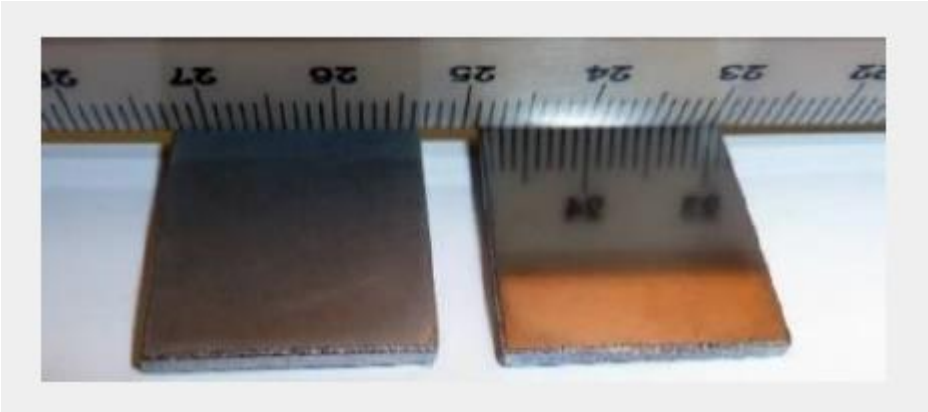
>> PEP is a chemically safe and low cost method.

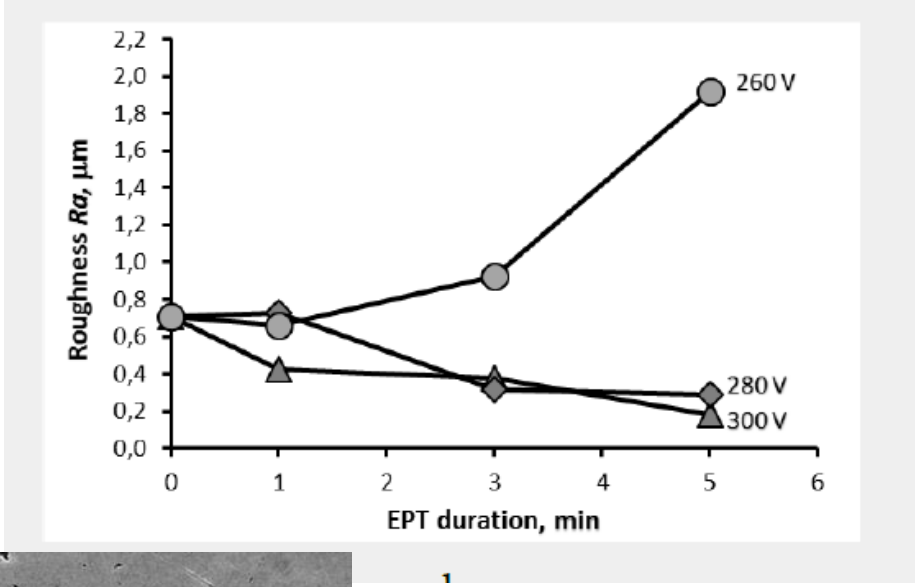


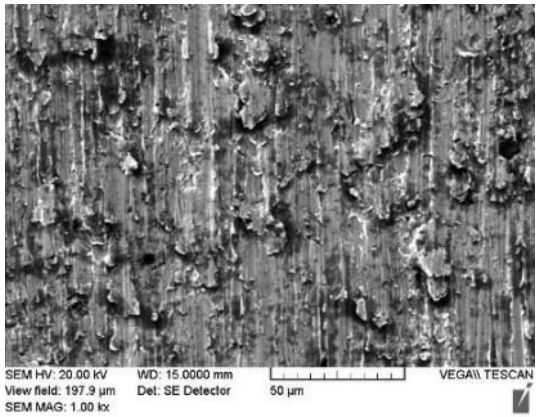
PEP for Nb (1)

Aliakseyeu, Y.; et al. *Sci. Tech.* **2018**, *17* (3), 211.
Aliakseyeu, Y.; et al. *Mechanika* **2021**, *27* (1), 88.

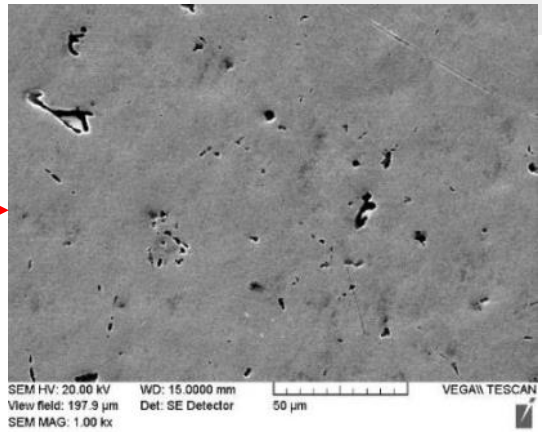
Electrolyte: 4% ammonium fluoride (NH_4F) aqueous solution.
Operation: ~300 V, ~0.20 A/cm^2.







PEP →



The pits are derived from mechanical polishing.

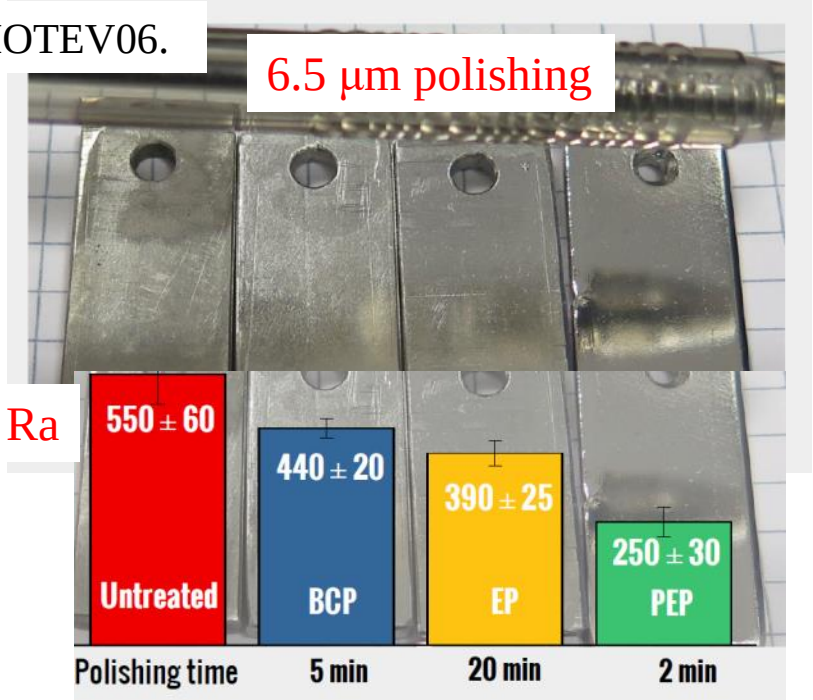
- This is a very promising result.
- However, we do not want to use ammonium fluoride.

PEP for Nb (2)

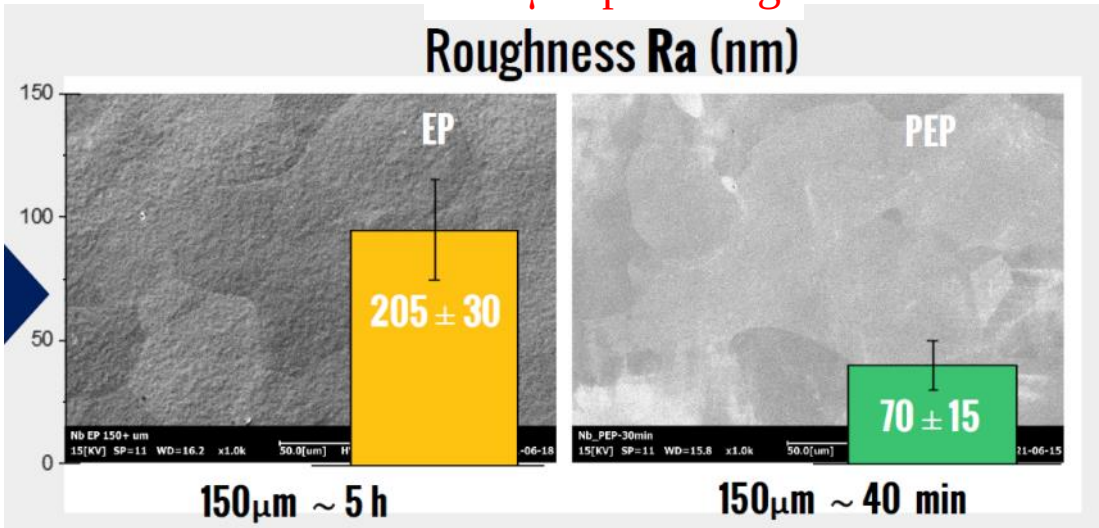
C. Pira; SRF2021, July 2021, THOTEV06.

PEP
Diluted salts
300 V
0.4-0.6 A/cm²
~150 W/cm²
3.5 µm/min (78℃)

- Salt: other than ammonium fluoride.
- being patented.



150 µm polishing

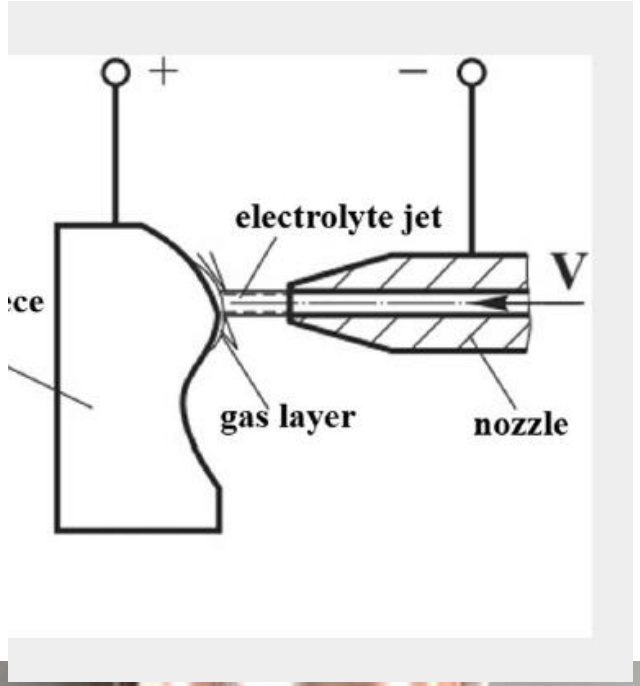


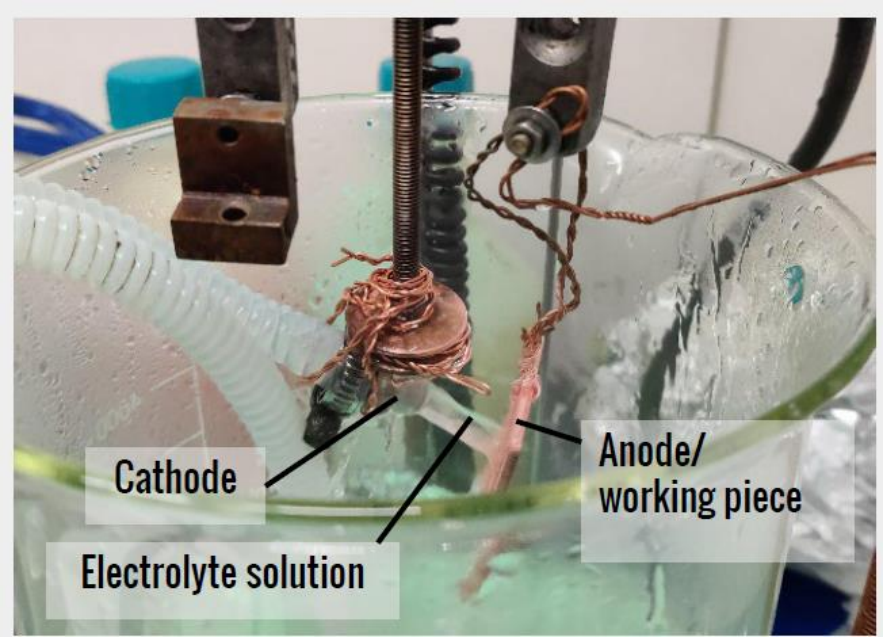
- The etching rate of PEP is 2 times faster than BCP and 10 times faster than HF-EP.
- Very smooth mirror surface.
- The crystal planes do not emerge even if the surface is etched a lot.

>> Applicable to polycrystal Nb.

Jet-PEP

C. Pira; SRF2021, July 2021, THOTEV06.

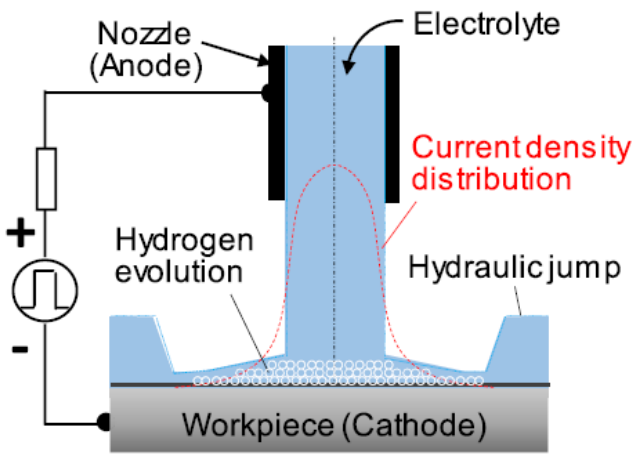




- It is difficult to polish the entire inner surface of 9 cell cavity at once by PEP method.
> Uniformity of the plasma state may be unattainable because of physical event.
> It requires a DC power supply with large capacity.
>> high cost and unsafe.
>> Jet PEP method is suitable for large surface to be polished.

Our future EP plan: Jet PEP for local polishing of Nb cavities

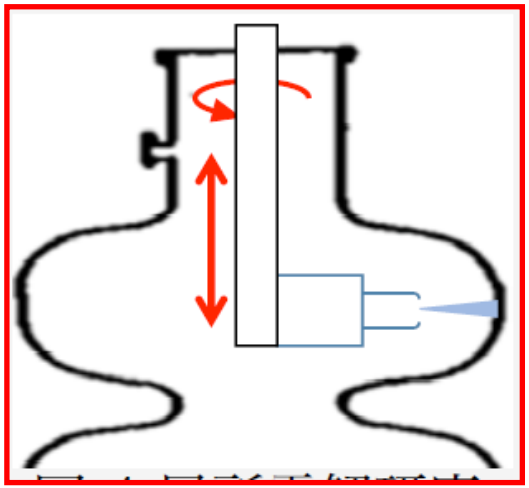
Jet EP



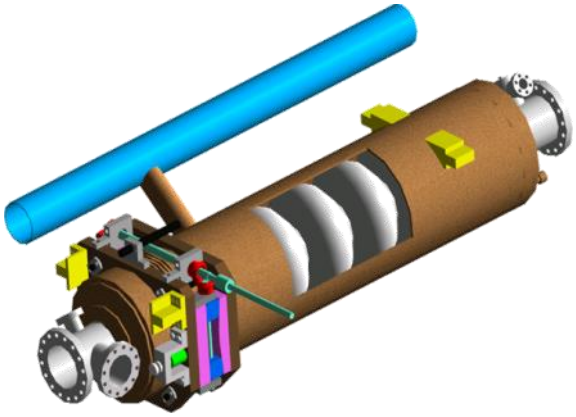
Zhao, Y.; Zhao, C.; Wang, S.; Kakudo, S.;
Kunieda, M. *Precis. Eng.* **2020**, *65* (1088), 259.

grinding Nb

Jet PEP for local polishing

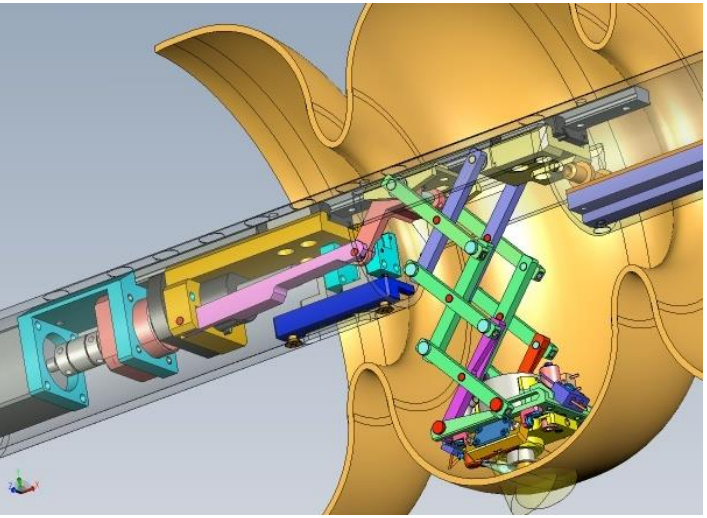


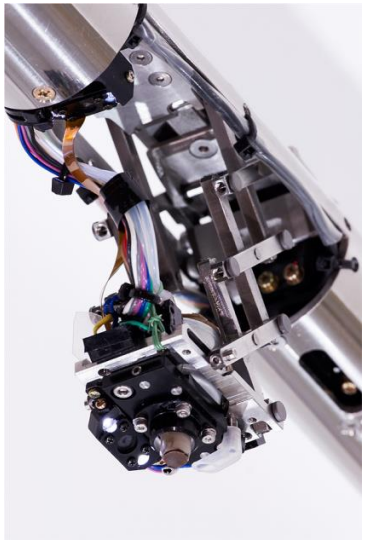
- Jet PEP method with a few % of aqueous salt solution (ammonium chloride?) is suitable for local polishing of Nb cavities.
  >> very safe and low cost.
- Unlike mechanical polishing,
  1) No metal shavings are left on Nb cavity surface.
  2) No stress strain occurs on the polished surface.
- Even a Nb cavity with Ti-jacket can be treated for Jet PEP.

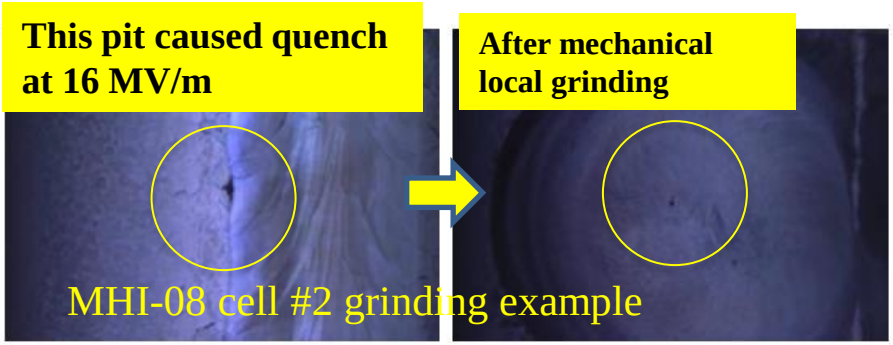


Mechanical local grinding + EP + Pre-tuning => Local Jet-PEP

Current mechanical local grinding machine with diamond powder compound







Grinding only for pit, without touching good surface

We have grinding dusts after mechanical local grinding. In order to remove the dusts, we need EP after local grinding. We also need pre-tuning to keep field-flatness after EP.

"Mechanical local grind + EP2 + Pre-tuning" can be replaced with "one Local Jet-PEP".

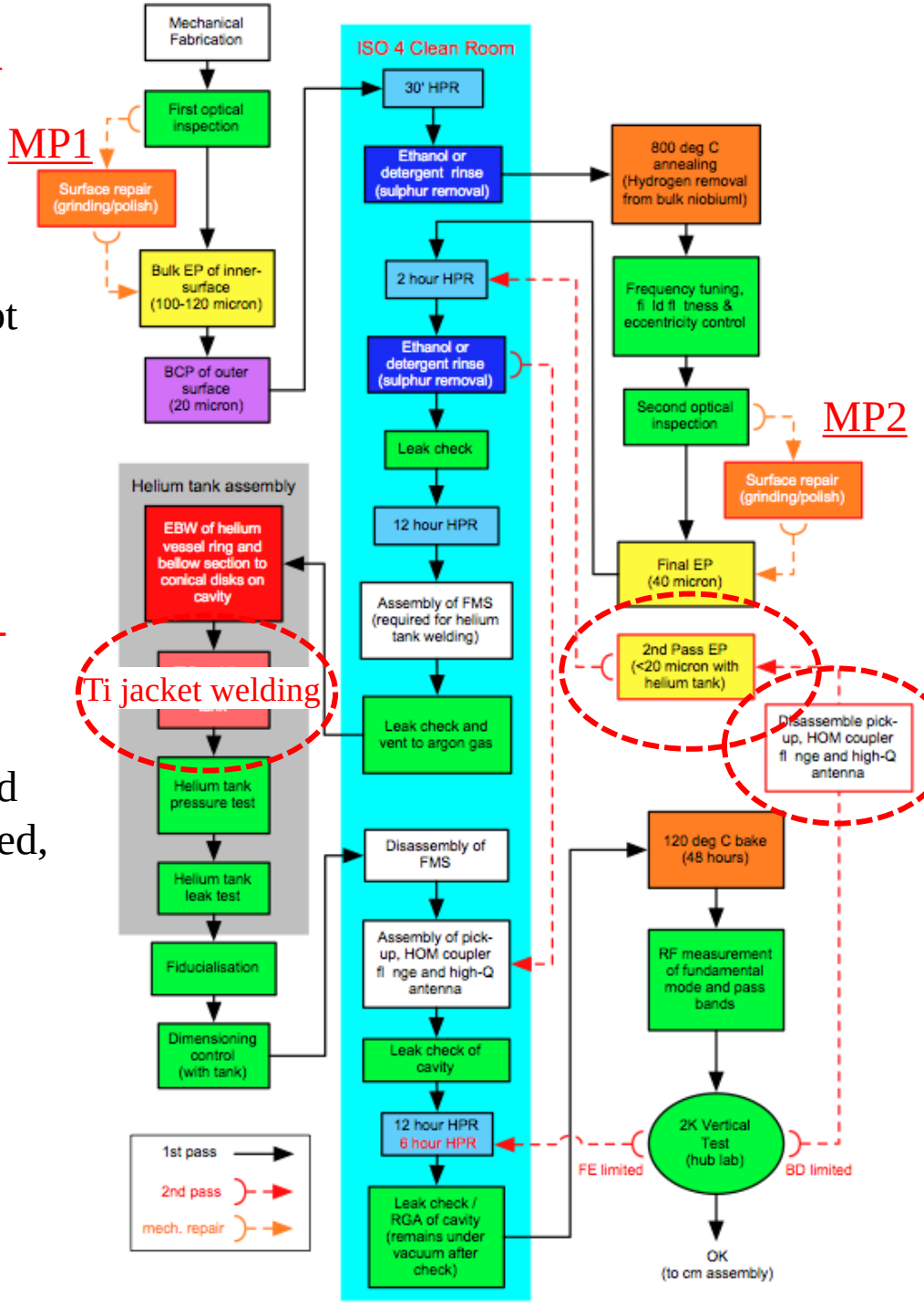
How does local Jet-PEP method works for fabrication of Nb cavities?

- The local Jet-PEP can be replaced with not only MP1 and MP2 but also EP2 and 2nd Pass EP.

- The local Jet-PEP is possible to apply to cavity with He jacket.

>> Moreover, it is possible to apply local Jet-PEP without removing antenna and so on.

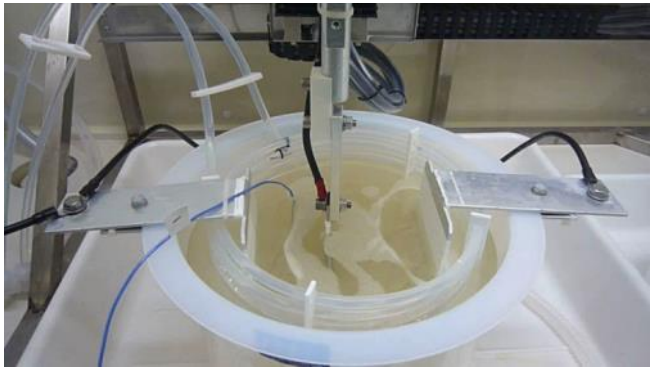
>> The number of cavities that are abandoned due to not enough SRF performance is reduced, and that improves the yield of cavity production and reduces costs for ILC.



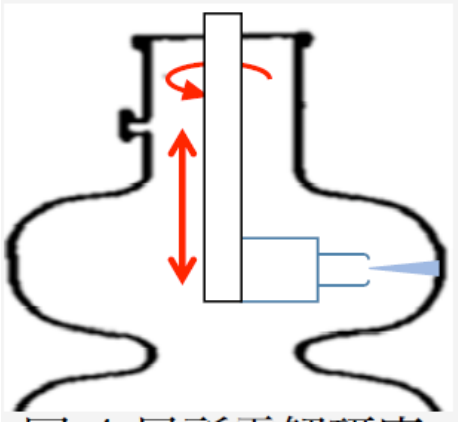
Conclusions

- Electrolytic polishing (EP) with HF electrolyte is an essential step in the surface treatment of Nb cavities.
- HF-EP is high cost due to the handling of HF electrolyte and the prevention of electrolyte leakage to the environment.
- We have been working on the establishment of the BP- and AC-EP methods as an HF-free EP. However, BP- and AC-EP methods were not energy efficient and took a long time to obtain flat Nb surface.
- Then, we just started to study the following new DC-EP methods.
  1) DC-EP with new electrolytes (a)NaCl in ethylene glycol, b)alkali aqueous solution)
  2) Jet PEP for local polishing of Nb cavities

HF-EP



Jet



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PEP

Development of hydrofluoric acid-free EP treatment of Nb cavities at KEK

Takeyoshi Goto, Takayuki Saeki (KEK)

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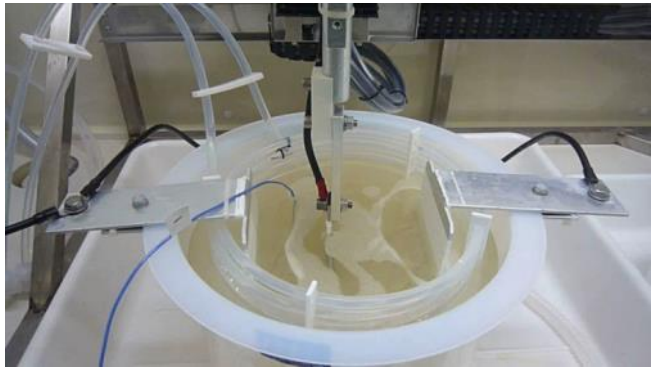
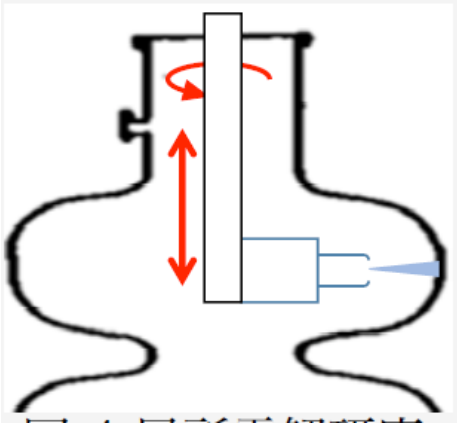
HF-EP



Jet



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PEP