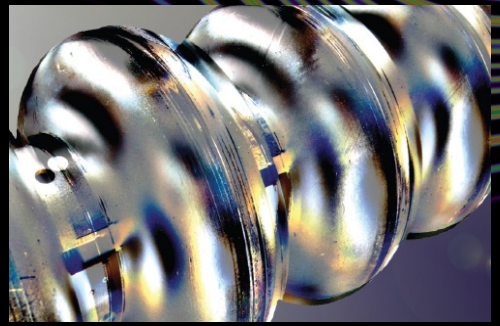
Surface Analysis of Niobium after Thermal/Gas Treatments via Samples

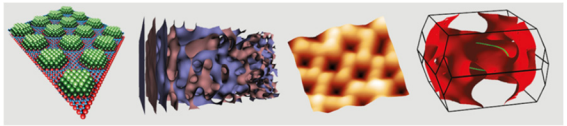


Review and recent results at DESY

A. Dangwal Pandey, G. D. L. Semione, C. Bate, S. Kulkarni, T. Keller, H. Noei, V. Vonk, J. Schaffran, M. Wenskat, D. Reschke, H. Weise, and A. Stierle

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

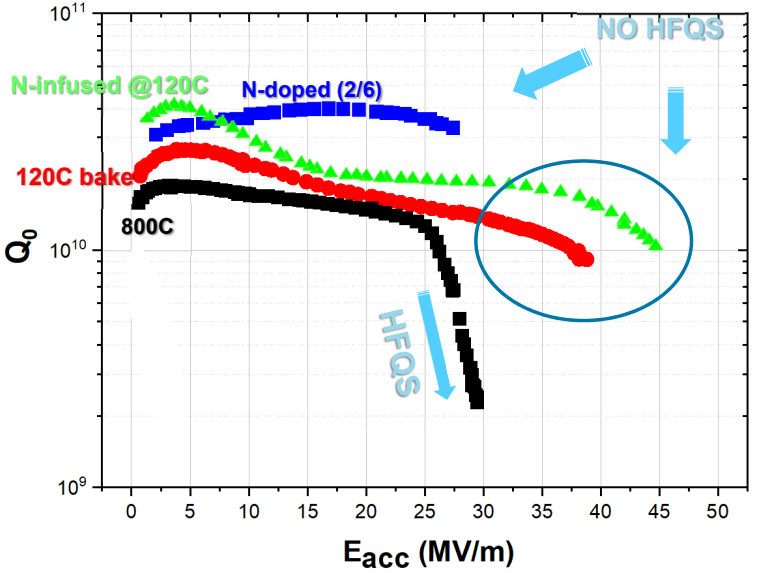
MML
From Matter to Materials and Life



MT ARD
MATTER AND TECHNOLOGIES
ACCELERATOR RESEARCH AND DEVELOPMENT

DESY.

Why do specific surface treatments lead to substantial changes in SRF cavity performance?



ZHSUNG, Fermilab | TTC Meeting at TRIUMF, February 05-08 2019

A. Grassellino et al., Supercond. Sci. Technol. 26 102001, (2013) & Supercond. Sci. Technol 30, 094004 (2017)

Final thermal treatment of SRF Nb cavities, reviewed here:

- **Low-T bake:** @120 °C (48 hrs)
  - Modified low-T bake: @ 75 °C (4hrs) +120 C (48 hrs)
- **N-infusion:** 800 °C (3 hrs) + @120 °C (48 hrs) in N_2

RF penetration depth lies within top 100 nm

Any change must happen at the surface.

A systematic investigation of Nb surface is needed

- to understand the **physics behind these processes,**
- to recognize the **key parameters in surface treatments**

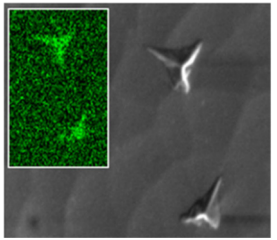
Extensive Nb sample R&D worldwide

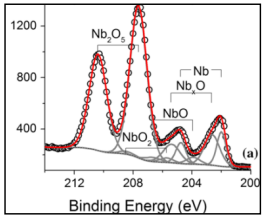
Towards cavities with highest quality factors (at high gradients)

Surface study of Nb with atomic details

Commonly used characterization methods:

- Microscopy: secondary electron microscopy (**SEM**), transmission electron microscopy (**TEM**), atomic force microscopy (**AFM**) etc.
- Spectroscopy: x-ray photo e spectroscopy (**XPS**), secondary-ion mass spectroscopy (**SIMS**) positron annihilation spectroscopy (**PAS**) etc.
- Diffraction: grazing incidence x-ray diffraction (**GIXRD**), nano electron diffraction (**NED**) etc.





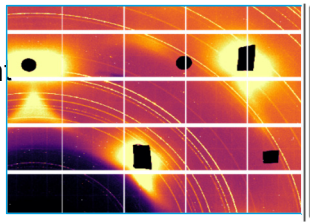
Different strategies:

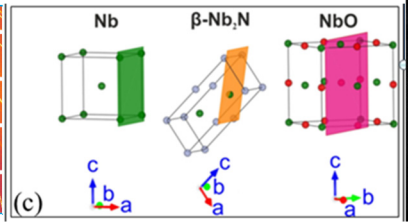
Ex-situ* characterization:** investigation ***after surface treatment

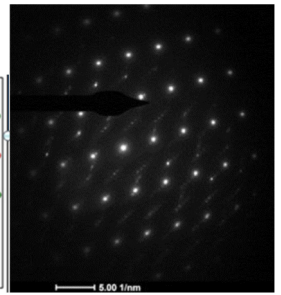
- Cavity cut-outs
- Samples treated *with* cavities
- Samples treated *similar to* cavities

In-situ* experiments:** investigation ***during surface treatment

- Samples treated *similar to* cavities







Extensive Nb sample R&D worldwide

Review of results reported from different labs within last 3 years

Nb samples investigated:

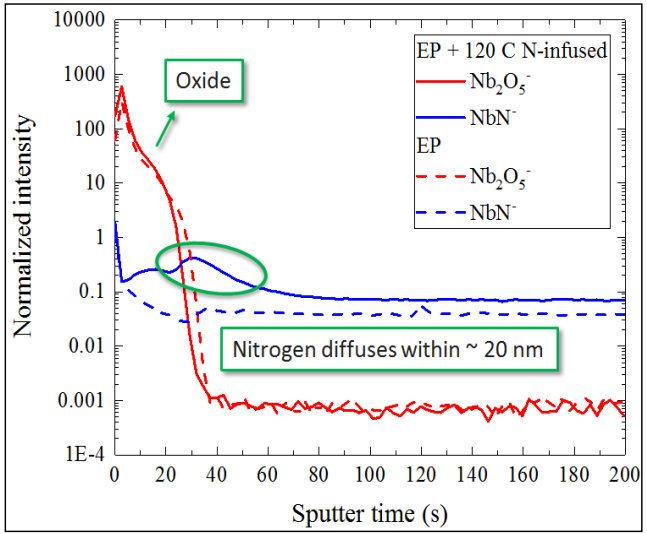
- **N-infusion**
- Thermal treatments without nitrogen
- Nb-carbide precipitates

Cut-outs of several cavities @ FNAL

TEM, SIMS, Cryo-AFM: identified NbH phases, confirmation of 'N' at metal-oxide interface, nanohydride segregation

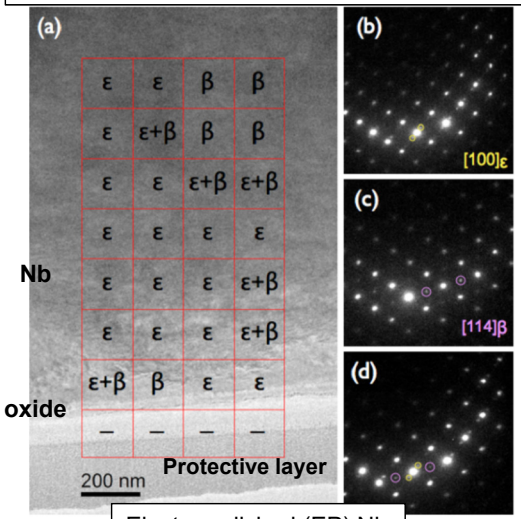
800°C/3hrs + 120°C in 25 mTorr N_2 /48hrs

Secondary Ion Mass Spectroscopy (SIMS):



- A. Romenenko, TTC meeting Riken Japan 2018

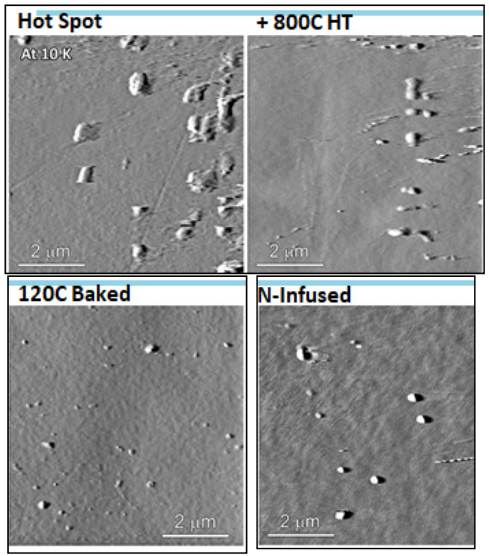
TEM **Electron diffraction**



Electro polished (EP) Nb

Y. Trenikhina *et al*, J. Appl. Phys. 117, 154507 (2015)

Cryo – AFM:



- ZHSung, TTC meeting at TRIUMF, Feb 2019

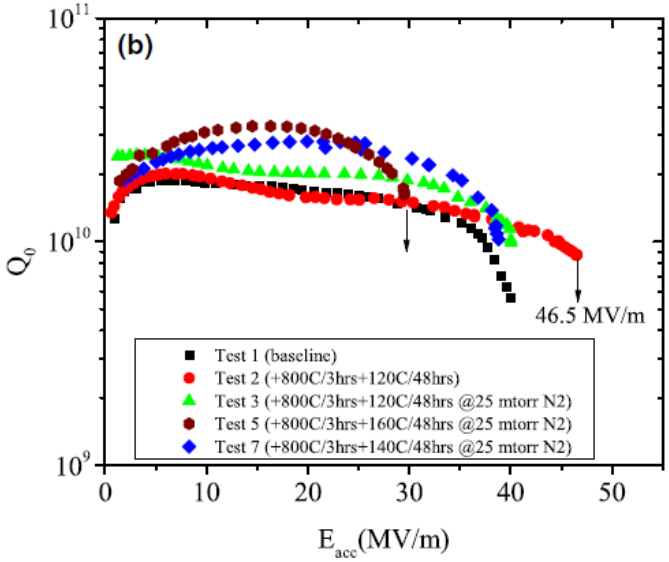
'N' present in N-infused Nb – N interstitials favorably trap H – suppress NbH segregation and thus suppress HFQS

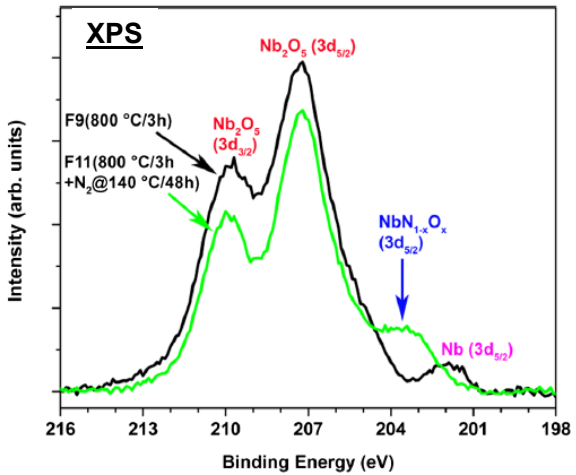
A. Romanenko *et al.*, IPAC 2018
M. Checchin *et al.*, IPAC 2018
[A. Grassellino talk this session]

N-infusion at varying T @ Jlab

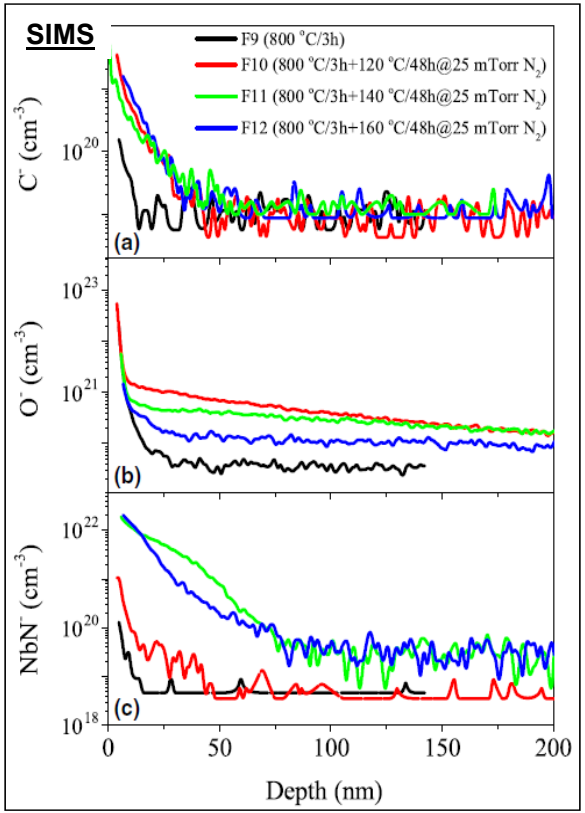
Fine grain Nb samples treated *similar to* cavities: XPS/SIMS/AC susceptibility measurements, 'N' containing phase

800°C/3hrs + inject N_2 @290°C + 120-160°C in 25 mTorr N_2 /48hrs





P. Dhakal *et al.* Phys Rev. Accel and Beams 21 (2018)



[P. Dhakal talk this session]

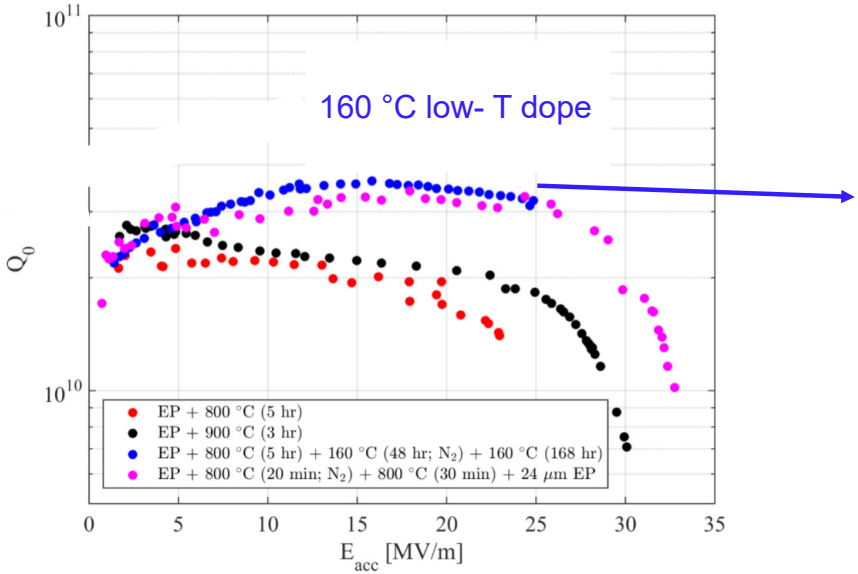
- a new chemical component observed, N excess within top 50 nm,
- in-line with level of dirtiness observed by AC susceptibility measurements

Nb oxy-nitrate phase present on Nb surface after 140°C -160°C N-infusion

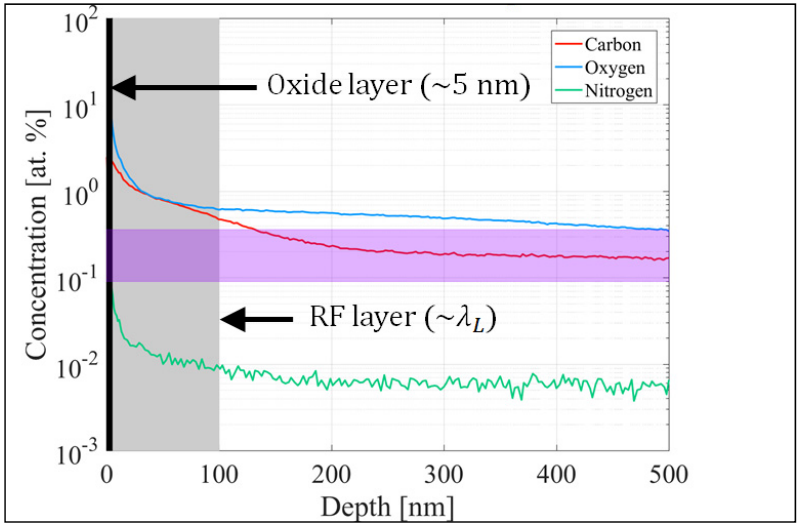
160°C N-infusion @ Cornell

Large grain Nb samples treated *with* cavities: SIMS, interstitials diffuse in to lattice, much higher C compared to N

800°C/5h + 160°C/48hrs in 40mTorr N_2 + 160°C bake 168 hrs



SIMS



P. N. Koufalis, M. Liepe, J. T. Maniscalco, TUXBA01, SRF2017.

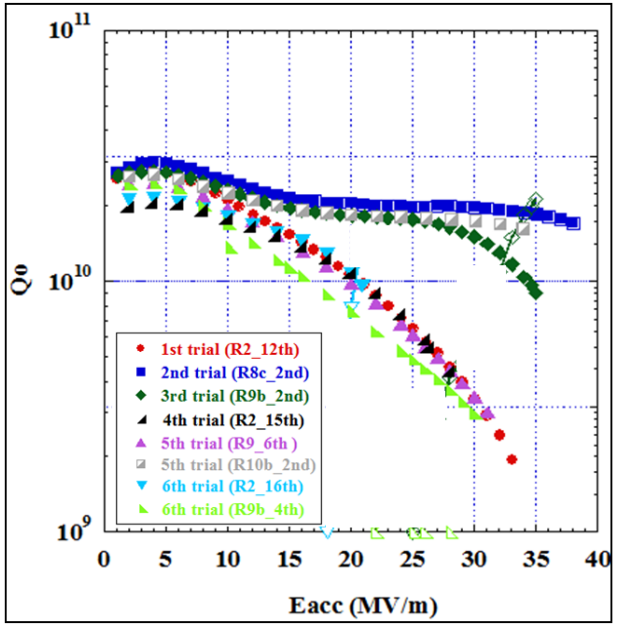
'N' observed only in top 5 nm, much higher C conc. in near-surface region

[J. T. Maniscalco talk this session]

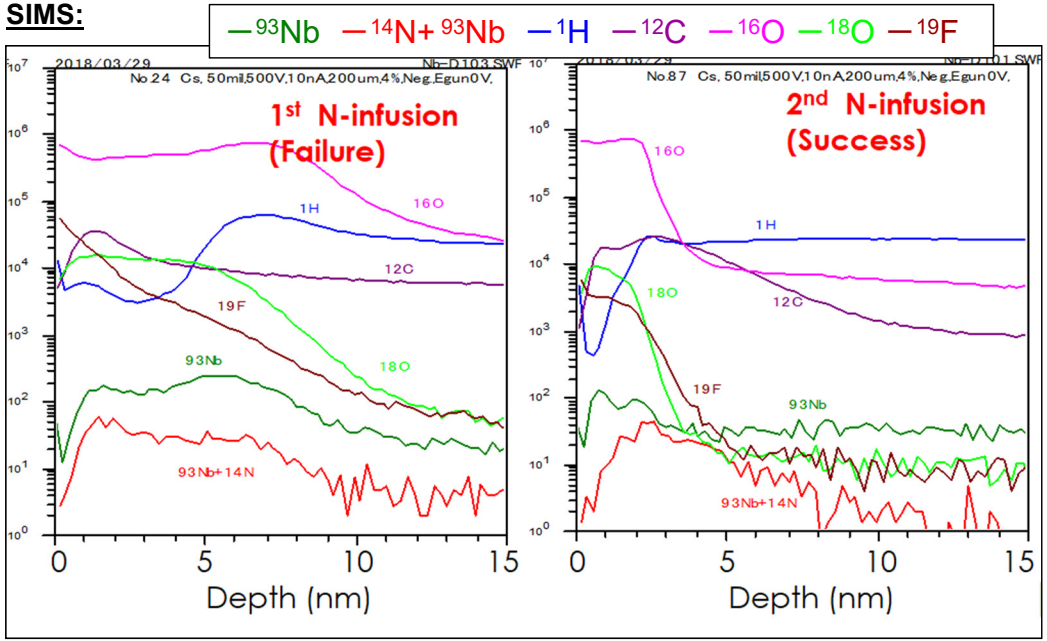
120°C N-infusion @ KEK

Fine grain Nb samples treated *with* cavities: SIMS/ EBSD/ SQUID/ SEM/ XPS , no clear indication of ‚N'

800°C/3hrs _+ 120°C in 25 mTorr N_2 /48hrs



SIMS:



" Oxygen and Carbon profiles seems to have the relationship with the maximum gradient and Q_o "

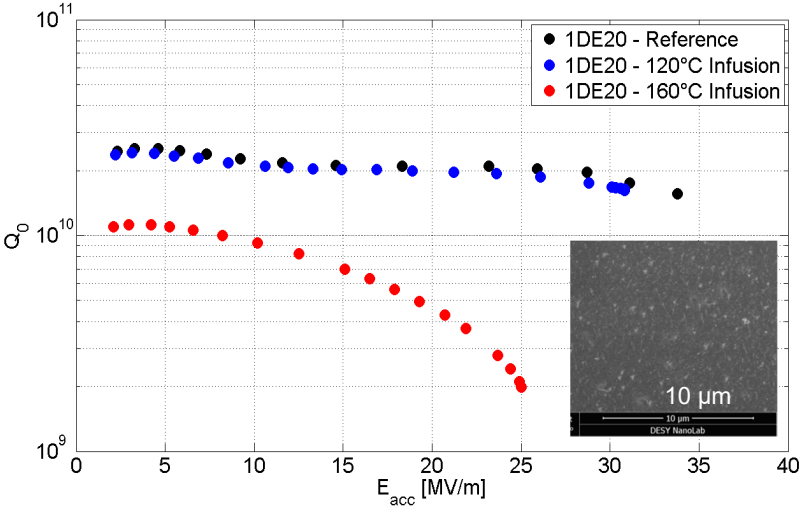
- by T. Konomi, TTC meeting Riken Japan 2018

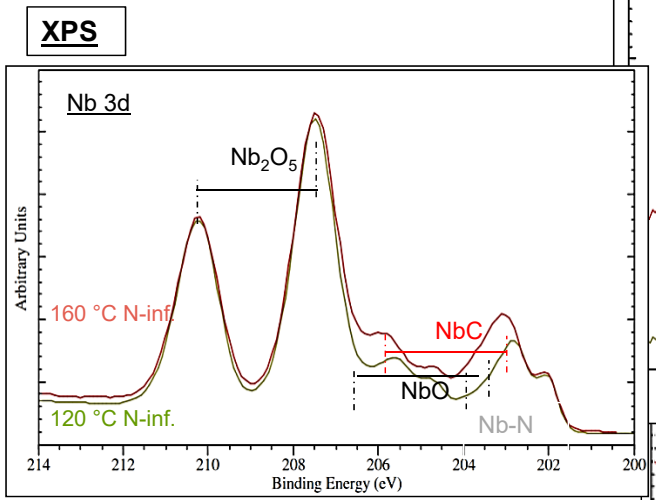
N-infusion at varying T @ DESY

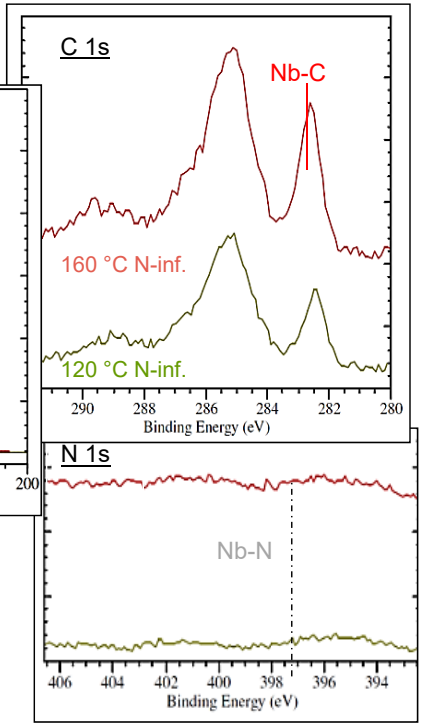
C. Bate, MOP023

Fine grain Nb samples treated *with* cavities: SIMS/ SEM/ XPS, more carbides on 160°C infusion, no indication of NbN

800°C/3 hrs + 120°C/25 m Torr N_2/ 48hrs ■
800°C/3 hrs + 160°C/25 m Torr N_2/48hrs ▲







- **SEM:** carbon rich precipitates for N-infused samples at 120 °C and 160 °C
- **XPS:** more Nb-C content for infusion @ 160 °C, no Nb-N bonding observed
- **SIMS:** more C for 160 °C infusion, no NbN identified

Higher carbide content for N-infusion at higher T could be related to failed cavity treatment

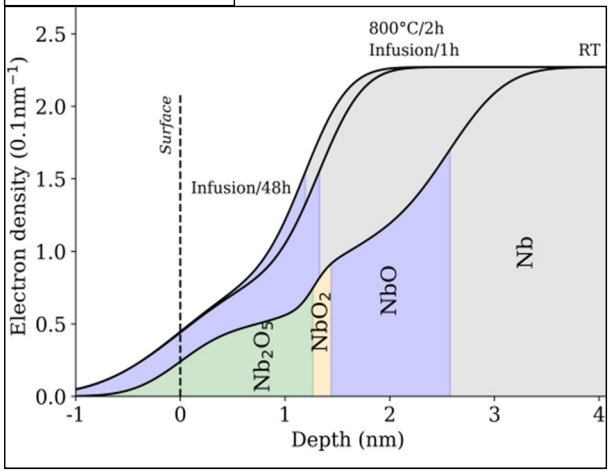
N-treatment of high purity single crystals @ DESY

GDL Semione, THP005

Nb(100) : *in-situ* X-ray reflectivity and grazing-incidence XRD @ high-energy (70 keV)

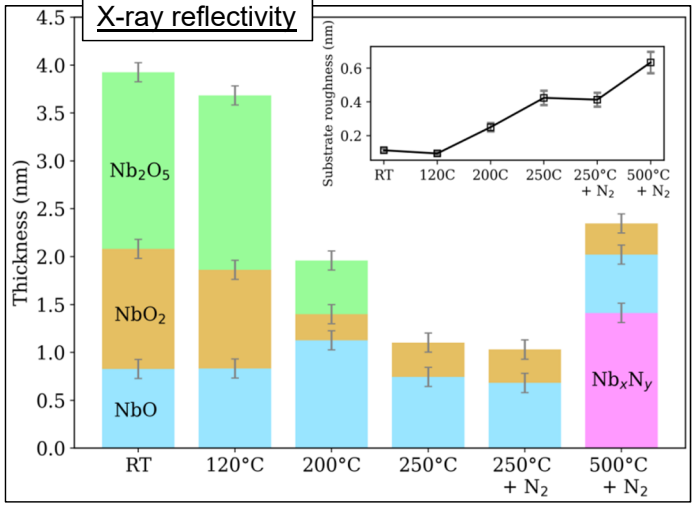
800°C/2hrs + 120°C in 25 mTorr N_2 /48hrs

X-ray reflectivity

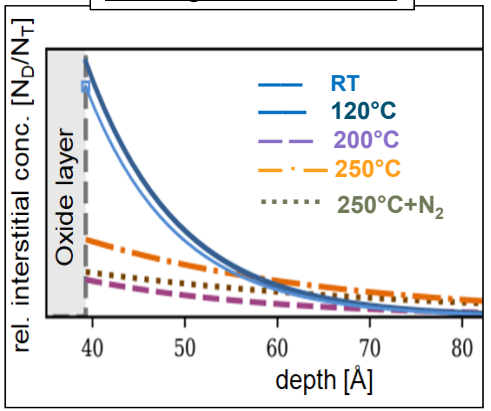


baking with/without, no prior 800°C anneal

X-ray reflectivity



Grazing-incidence XRD



N –infusion: unchanged surface layers @ 120 °C before and after infusion

Baking in N_2: @ 120°C – slight decrease in oxide thickness and roughness
@ 250 °C – NbO and NbO_2 present,
@ 250 °C + N_2 – interstitial conc. doesn't increase at metal oxide interface
@ 500 °C + N_2 – NbO and NbO_2 present, Nb_xN_y formed

Increased performance of SRF cavities after N-treatment at low T is related to real cavity material's properties such as grain boundaries and its higher level of impurities.

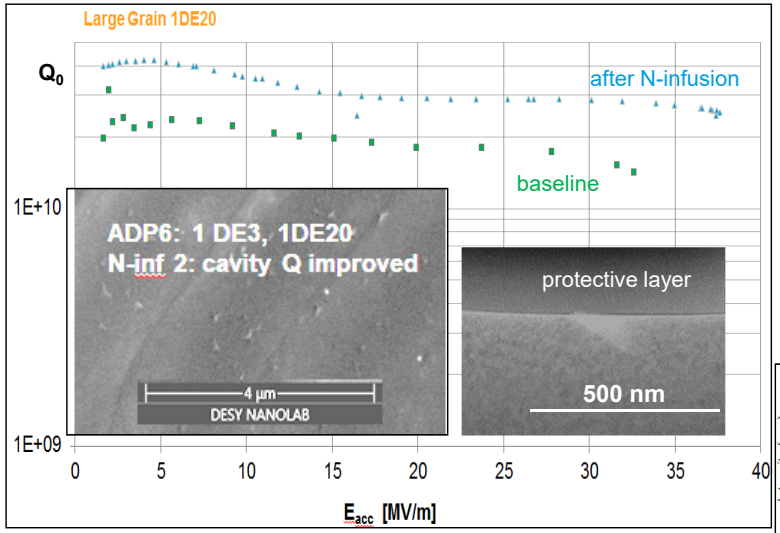
GDL Semione *et al.*, http://arxiv.org/abs/1906.11530 submitted to PR B

N-infusion in FNAL, sample investigation @ DESY

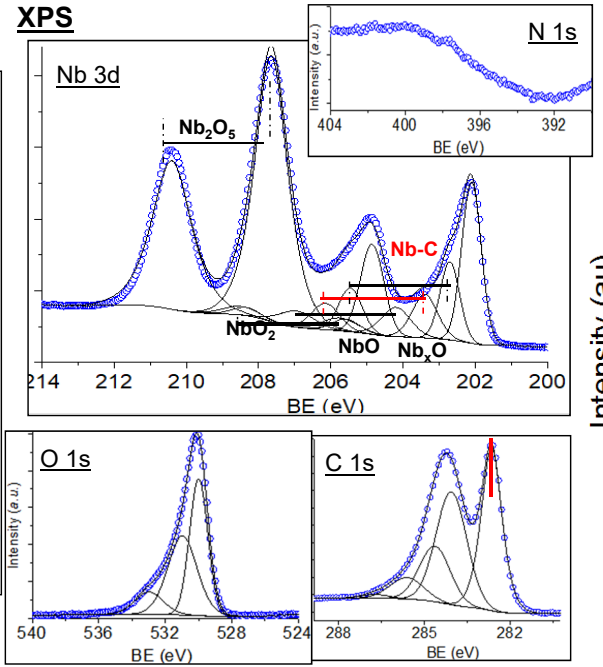
A. Dangwal Pandey

Large grain Nb (100) sample: SEM/XPS/SIMS, shallow NbC precipitates, absence of Nb-N

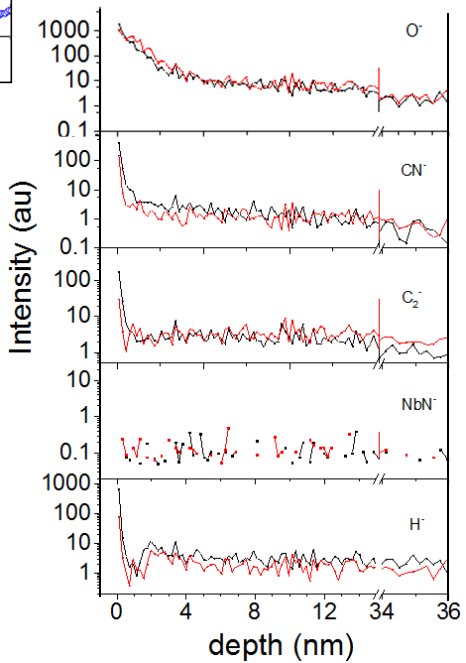
800°C/3hrs + 120°C in 25 mTorr N_2 /48hrs



XPS



SIMS



Sample corresponding to a successfully infused cavity:

C-precipitates still present but **very shallow**

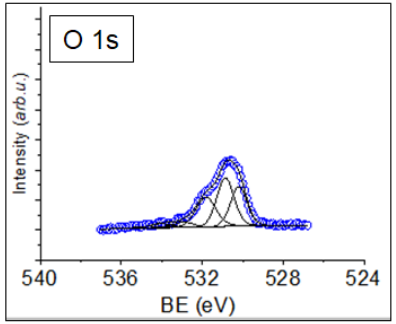
No signature of 'N' containing phase on N-infused Nb

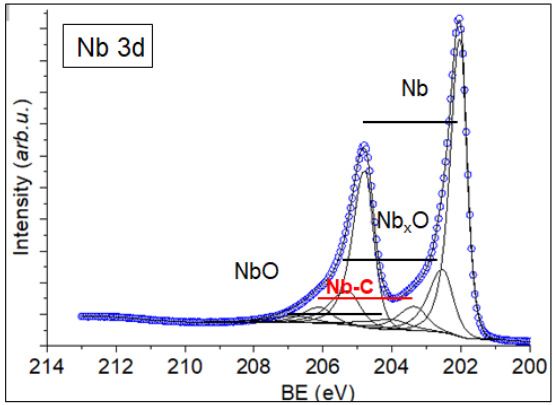
N-infusion at very low N_2 pressure @ DESY

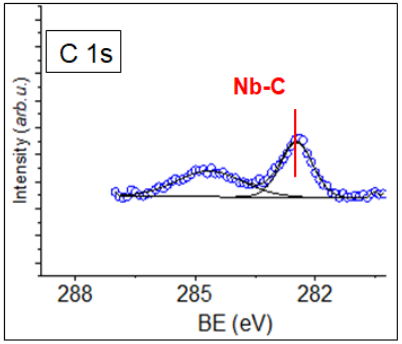
A. Dangwal Pandey

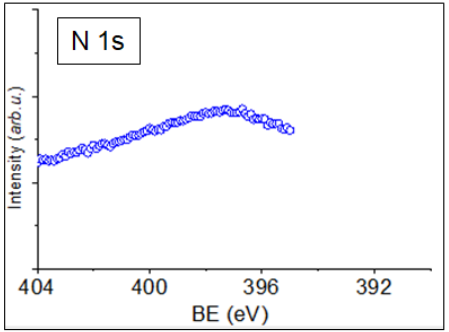
Large grain Nb (100) sample: *in-situ* XPS experiment, Nb-N observed

In-situ XPS:









800 °C + 120°C/12 hrs in UHV (no N_2)

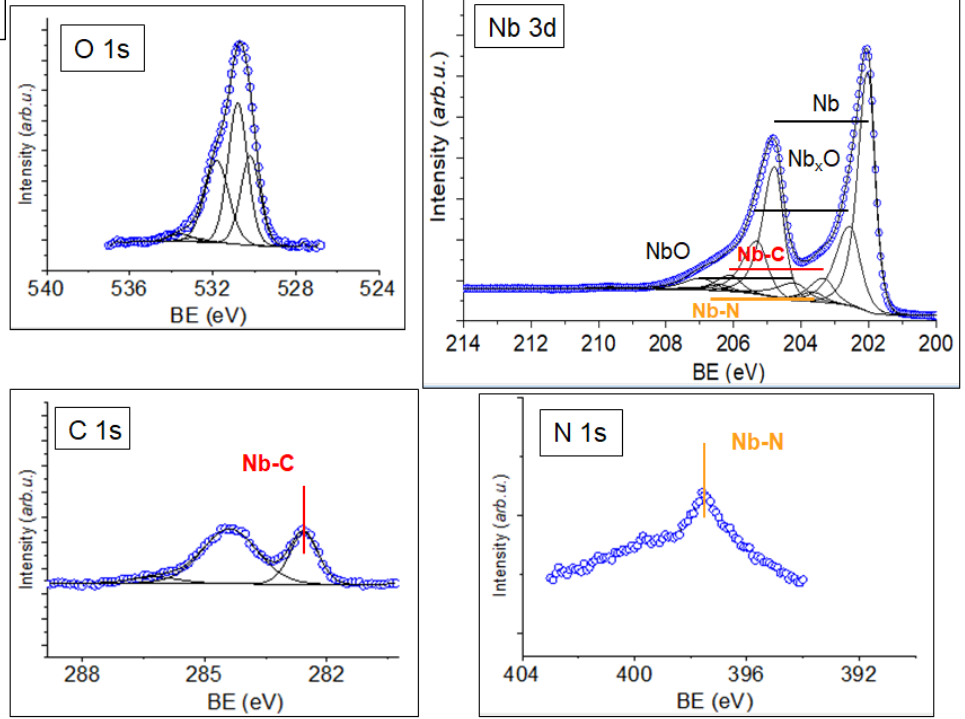
- NbO, NbC present on surface
- No Nb-N observed

N-infusion at very low N_2 pressure @ DESY

A. Dangwal Pandey

Large grain Nb (100) sample: *in-situ* XPS experiment, Nb-N observed

In-situ XPS:



800 °C + 120°C/12 hrs in UHV (no N_2)

- NbO, NbC present on surface
- No Nb-N observed

+ 120 °C in N_2 (0.004 m Torr)/13 hrs

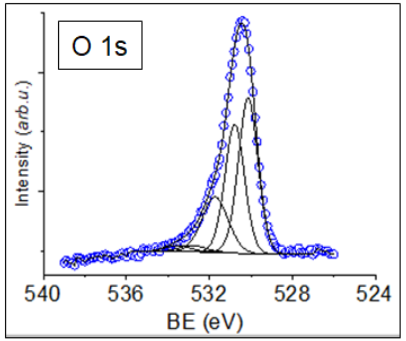
- NbO grows further
- NbC still visible
- Nb-N observed in top 10 nm surface

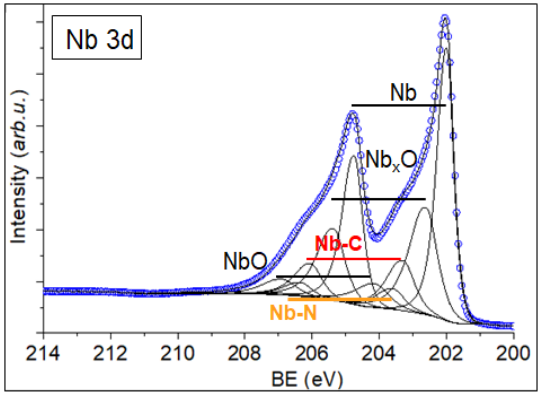
N-infusion at very low N_2 pressure @ DESY

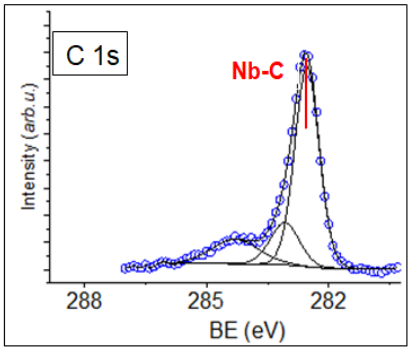
A. Dangwal Pandey

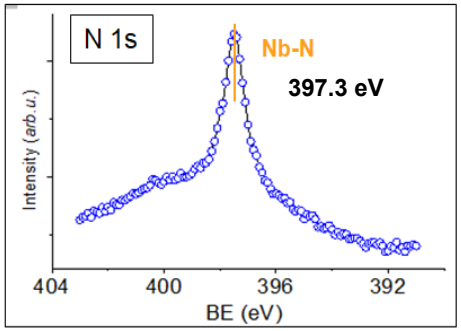
Large grain Nb (100) sample: *in-situ* XPS experiment, Nb-N observed

In-situ XPS:









800 °C + 120°C/12 hrs in UHV (no N_2)

- NbO, NbC present on surface
- No Nb-N observed

+ 120 °C in N_2 (0.004 m Torr)/13 hrs

- NbO grows further
- NbC still visible
- Nb-N observed in top 10 nm surface

@ 500°C heated in UHV to remove N
+ 260°C 12 hrs

+ 260°C in N_2 (0.004 mTorr)/15 hrs

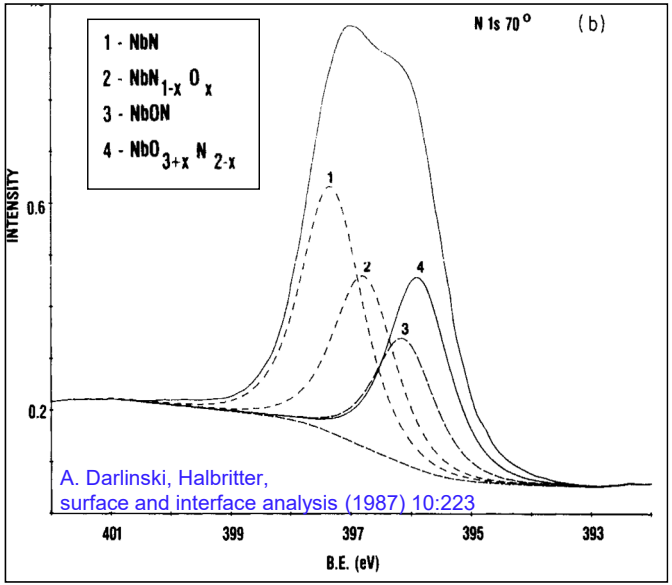
Nb-N peak got intense by N-infusion at 260 °C

N-infusion at very low N_2 pressure @ DESY

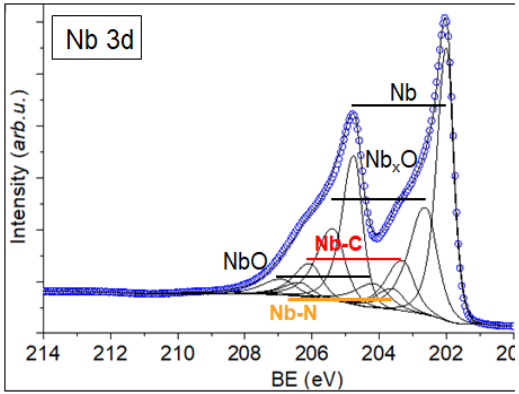
A. Dangwal Pandey

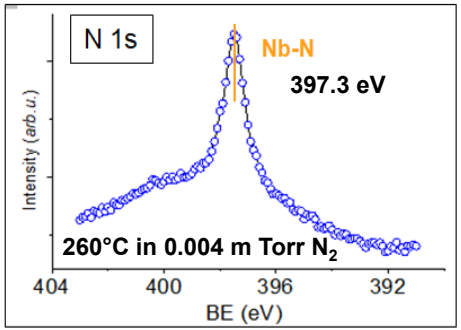
Large grain Nb (100) sample: *in-situ* XPS experiment, Nb-N observed

NbN: formed by nitridation of large grain Nb @ 620°C, Oxidized in air for 30 min.

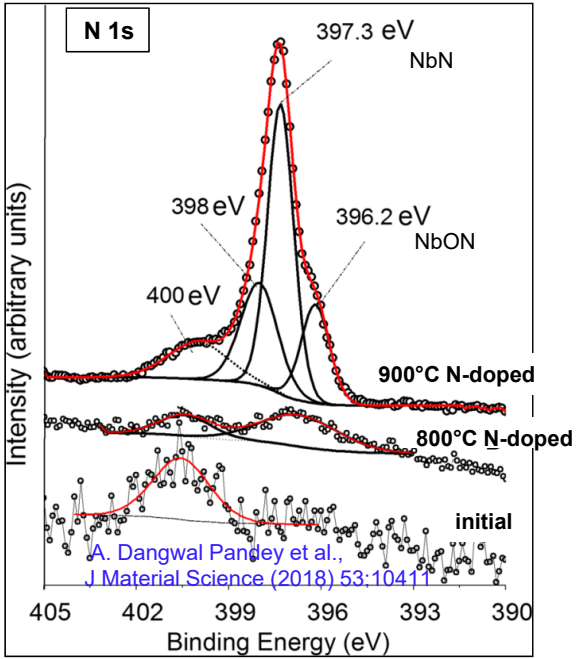


A. Darlinski, Halbritter, surface and interface analysis (1987) 10:223





NbN: formed by nitridation of fine-grain Nb @ 900°C, Oxidized in air for few months.



A. Dangwal Pandey et al., J Material Science (2018) 53:10411

N-infusion at very low N_2 pressure @ DESY

A. Dangwal Pandey

Large grain Nb (100) sample: *in-situ* XPS experiment, Nb-N observed

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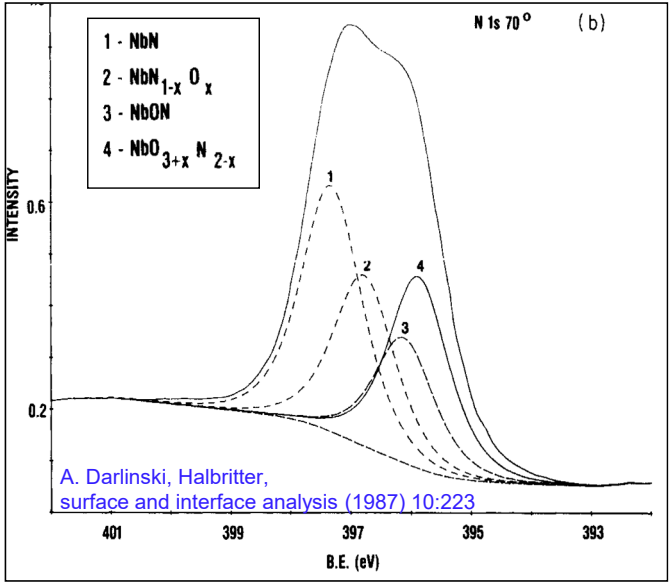
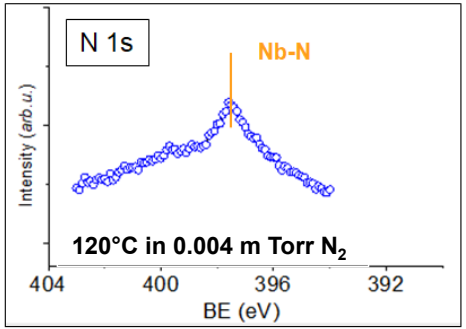
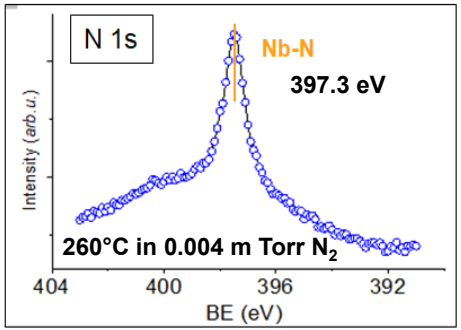
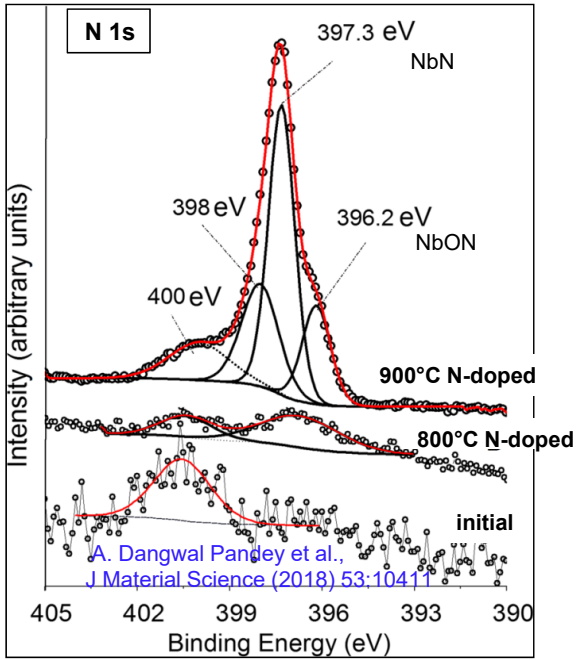


A. Darlinski, Halbritter, surface and interface analysis (1987) 10:223





NbN: formed by nitridation of fine-grain Nb @ 900°C, Oxidized in air for few months.



A. Dangwal Pandey et al., J Material Science (2018) 53:10411

Fully covered surface oxide layer suppresses signals from material underneath in earlier XPS investigations performed e*x-situ*.

Clear indication of NbN phase formed in 0.004 mTorr N_2 partial pressure at 120°C

Extensive Nb sample R&D worldwide

Review of results reported from different labs within last 3 years

Nb samples investigated:

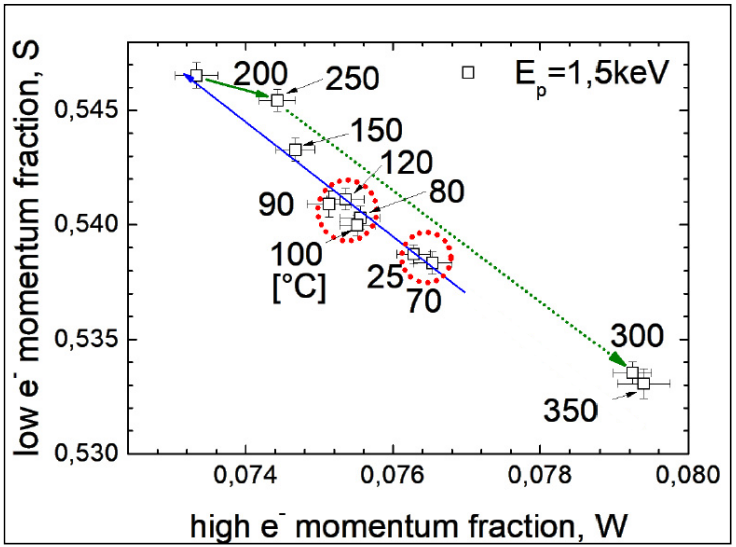
- N-infusion at low T (below 300°C)
- **Thermal treatments without nitrogen**
- Nb-carbide precipitates

low T bake study @ DESY

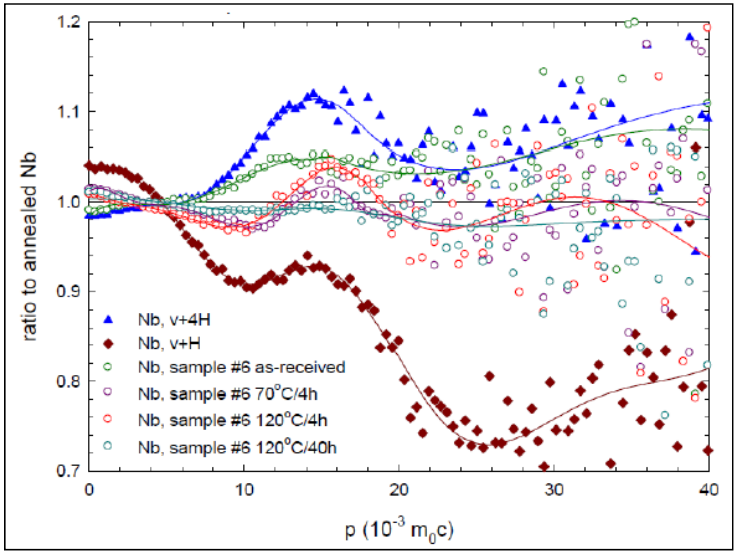
M. Wenskat, MOP024

Fine grain Nb samples: Positron annihilation spectroscopy (PAS), vacancy-hydrogen dynamics during

Low – T bake : Vacancy evolution with temperature



formation of v+nH complexes for low-T bake



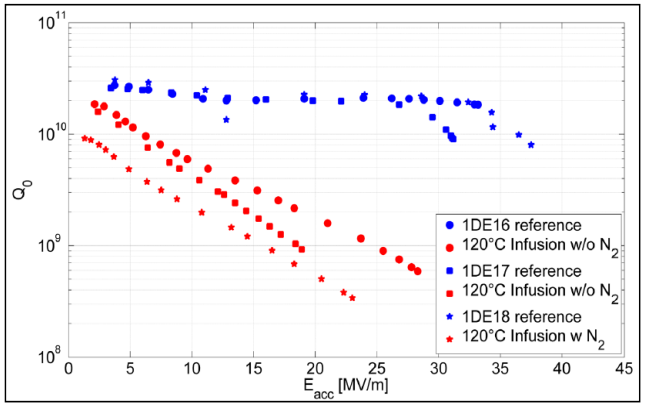
Vacancy-Hydrogen complexes are influenced by the baking procedures

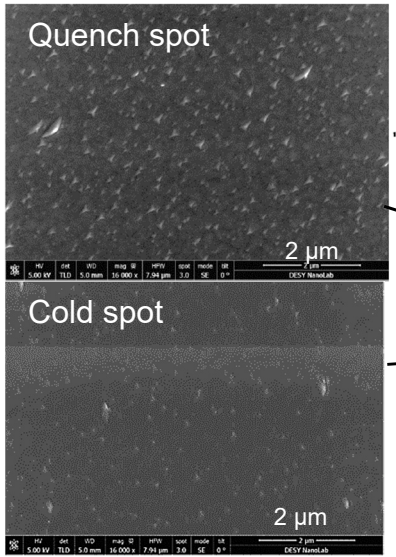
Cavity cut-outs @ DESY

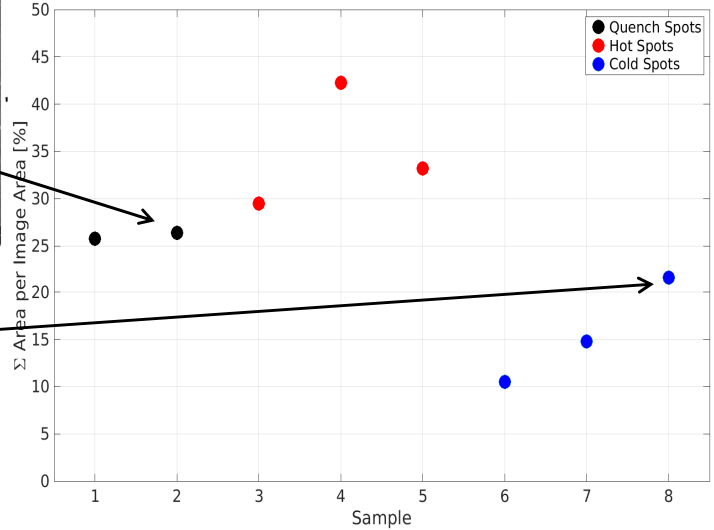
M. Wenskat, MOP025

Case study of a failed infusion– SEM/SIMS/EBSD - Nb-carbide precipitates

Cavity treatment: 800°C 3 hrs + 120°C 48 hrs







Hot spots and quench spots:

SEM: Niobium Carbides are denser and larger

SIMS: higher Carbon-Signal in the first ~20nm

Size and density of carbides detrimental for RF performance

Extensive Nb sample R&D worldwide

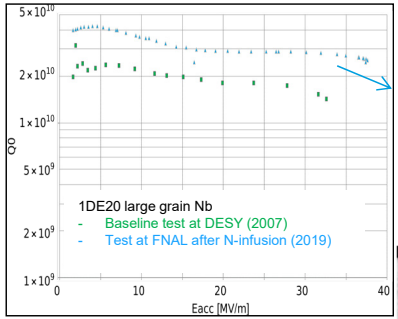
Review of results reported from different labs within last 3 years

Nb samples investigated:

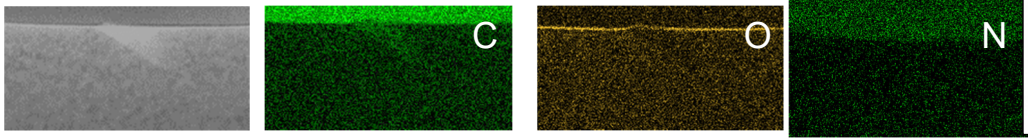
- N-infusion at low T (below 300°C)
- Thermal treatments without nitrogen
- **Nb-carbide precipitates**

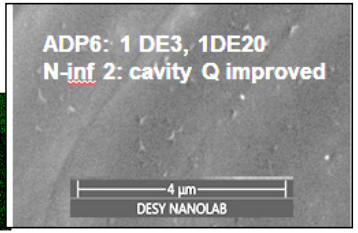
Carbon-rich precipitates on cavity related samples

FIB lamella, Energy dispersive x-ray analysis, Electron backscatter diffraction (EBSD)

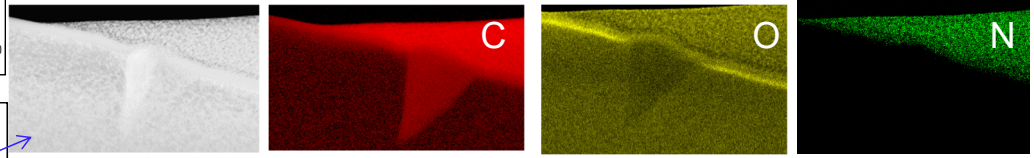


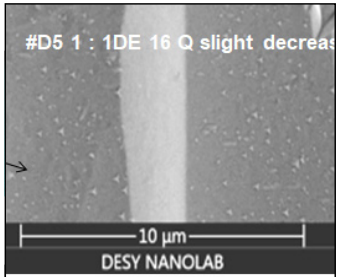
Cavity improved after N-infusion @FNAL

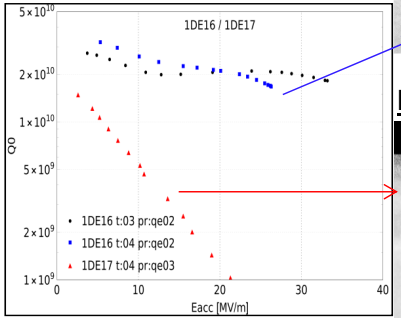




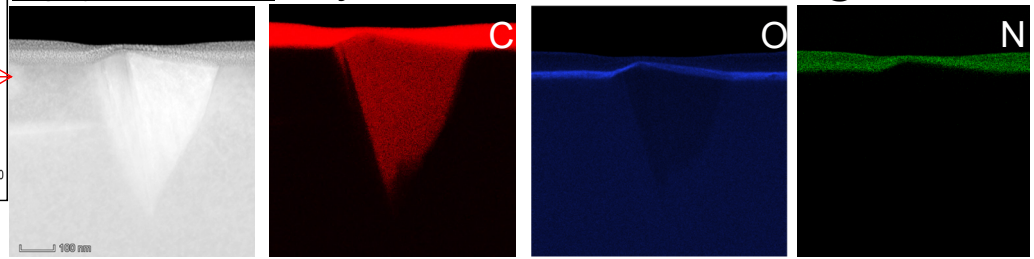
Still good cavity performance after heat treatment 800 °C +120°C @DESY

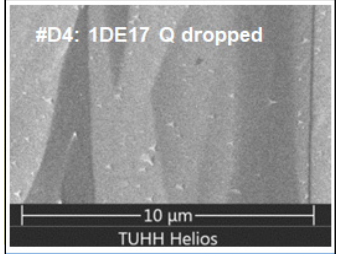






Highly deteriorated cavity after heat treatment 800 °C +120°C @DESY



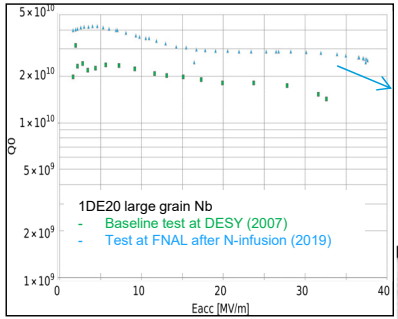


BCP Nb(221), thermally treated at DESY
#D5: 3h@800°C/48h@120°C without N2
#D4: 2h@800°C/48h@120°C without N2

Larger and deeper **saw-tooth like precipitates** on heavily deteriorated cavities

Carbon-rich precipitates on cavity related samples

FIB lamella, Energy dispersive x-ray analysis, Electron backscatter diffraction (EBSD)



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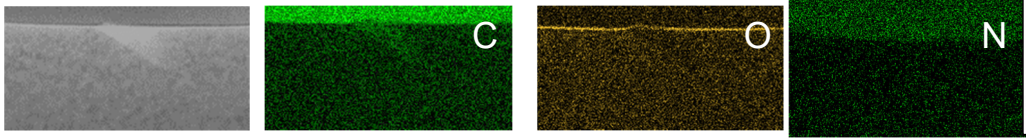
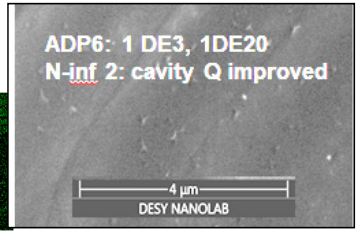
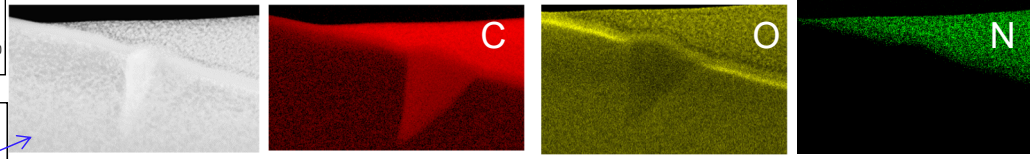
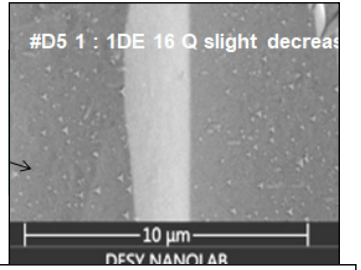
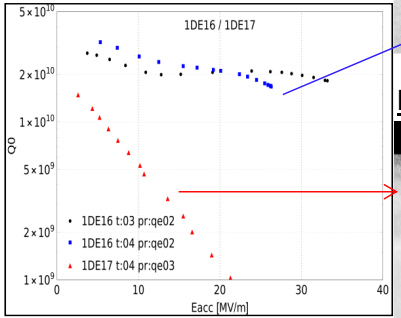




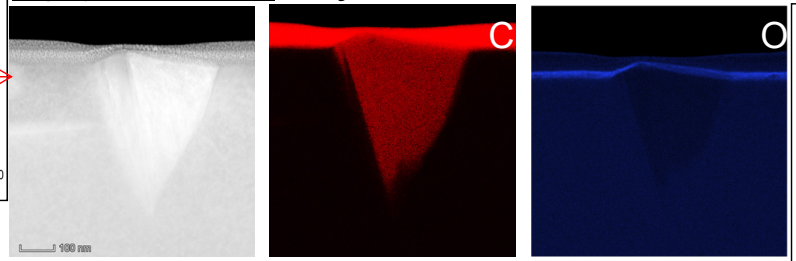
Still good cavity performance after heat treatment 800 °C +120°C @DESY



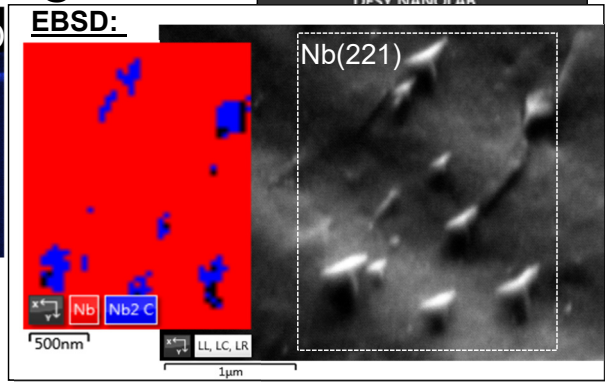




Highly deteriorated cavity after heat treatment 800 °C +120°C @DESY



EBSD:



Larger and deeper **saw-tooth like precipitates** on heavily deteriorated cavities

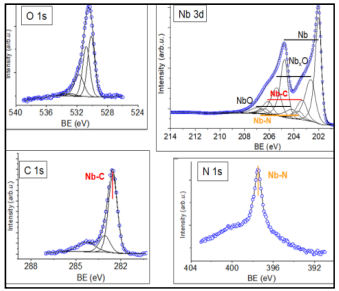
Nb_2C phase confirmed

Posiible sources of C: surrounding environment, bulk Nb – not seen on high purity Nb single crystals

Summary:

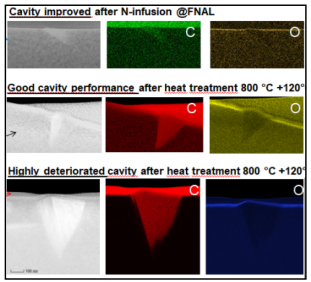
- **Review of Nb surface analysis worldwide**
- **N-infusion: contradictory findings on presence of Nb-N from different labs by *ex-situ* meas.**
  - **NbN** signal reported by FNAL (20 nm), Jlab (50 nm), Cornell (5 nm) using **SIMS**,
  - could not be observed by KEK and DESY in *ex-situ* **XPS** and **SIMS,** and *in-situ* **XRD** experiments

  BUT… different experimental conditions, different infusion recipes, and different Nb material



- **Confirmation of N bound to Nb after 120°C N-infusion at low pressure by *in-situ* XPS**
  - N_2 partial pressure three orders of magnitude lower than that used for cavities
  - If Nb-N is formed at the interface, possibility of N going into Nb lattice

- **Low-T bake without Nitrogen**
  - Vacancy evolution with T and vacancy-hydrogen complex formation studied by means of **PAS**



- **Carbon –rich precipitates observed for treatments with/without N_2**
  - Observed on samples treated with cavities as well as on cavity cut-outs
  - larger and deeper precipitates <-> worse cavity performance
  - **Nb_2C phase** – unambiguously identified

Challenge: to identify and deconvolute the role of
- **NbN, NbC, NbO phases on surface and**
- **interstitials C, N, O in Nb lattice**

whether impurities in cavity-grade Nb promotes N-diffusion into Nb ?

Acknowledgements

- **Colleagues at Cornell, FNAL, Jlab, KEK for the collaboration**
- **BEEM (electron microscopy) group at TUHH**
- **DESY Nanolab team** and **MSL/MPL group** at DESY

Thank you very much for your attention!