Electrochemical Bronze Route for SRF Cavities

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This research is funded by DOE Accelerator Stewardship Program: DE-SC0018379

Project Objective of Multi-Institute Research Team

- **Main objective**
  - explore enabling processes for thin film Nb_3Sn SRF cavity technology
  - identify challenges and understand underlying mechanism behind each challenge
- **Research team**
  - Overall lead: NHMFB/FSU
  - Cavity structure and production: BTM
  - PVD route: NHMFB/FSU
  - Electrochemical route: UT Arlington
- **At Nb_3Sn SRF2020**
  - PVD route and Nb_3Sn growth study: presentation by Dr. W. Withanage
  - this presentation: SRF by electrochemical method

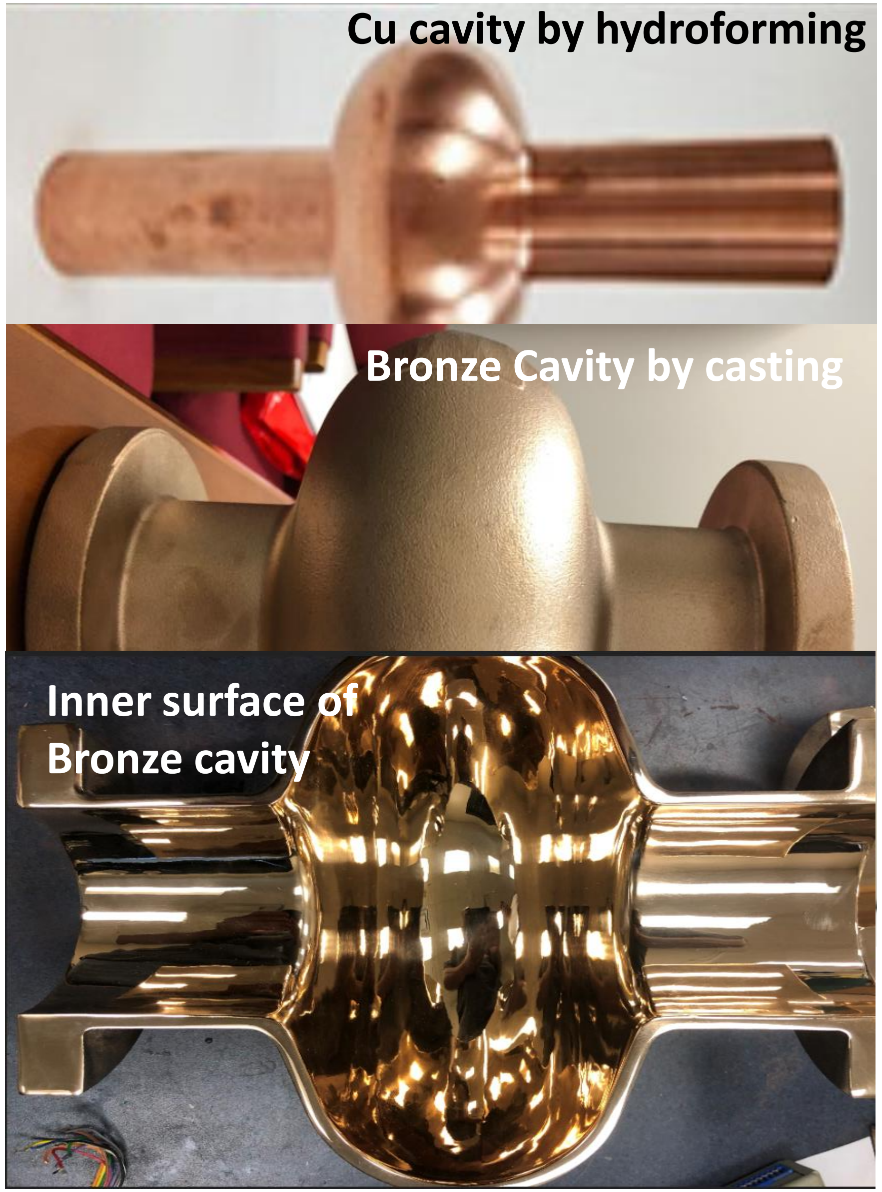
Fermi Lab 9-cell Nb SRF

Research Motivation: Seamless Thin Film SRF Cavity

- **Seamless thin film SRF cavity**
  - next generation SRF cavity technology
  - high electrical and thermal conductivity
  - cost effective production and operation when realized

- **Nb_3Sn by Bronze route**
  - Nb_3Sn is well utilized superconducting phase
  - Nb_3Sn can be of thin film
  - bronze route can enable formation and growth of thin film Nb_3Sn at ~700C.

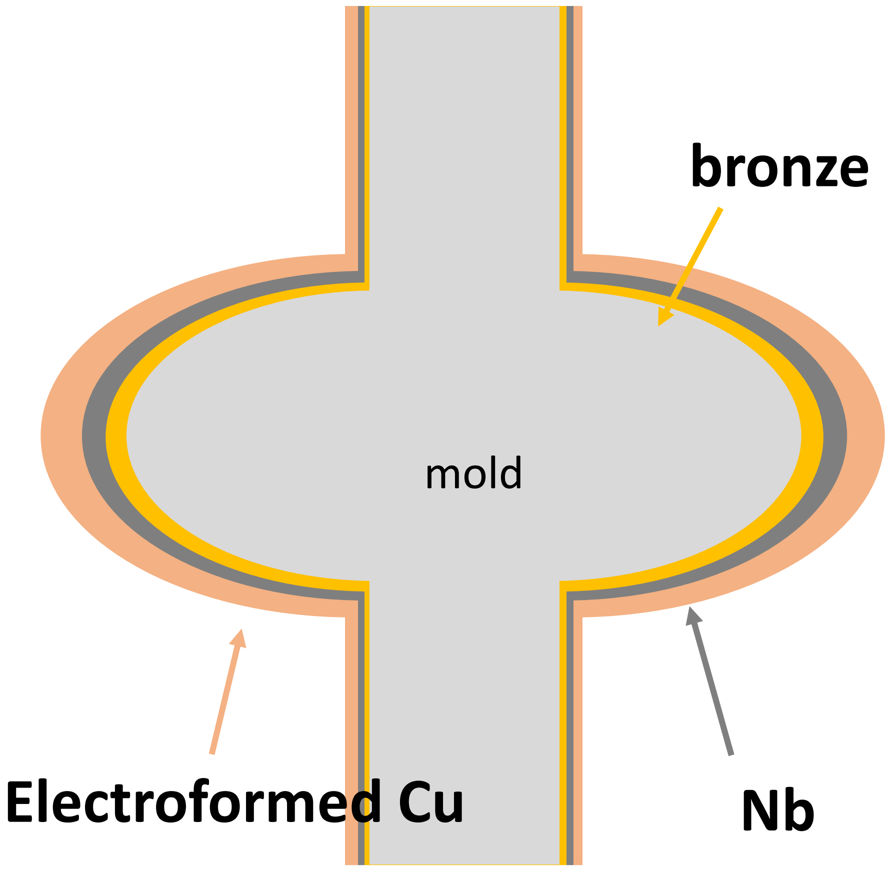
- **Various process routes and form factors**
  - Nb thin film on bronze cavity.
  - Nb/bronze thin film on Cu cavity



Produced by BTM

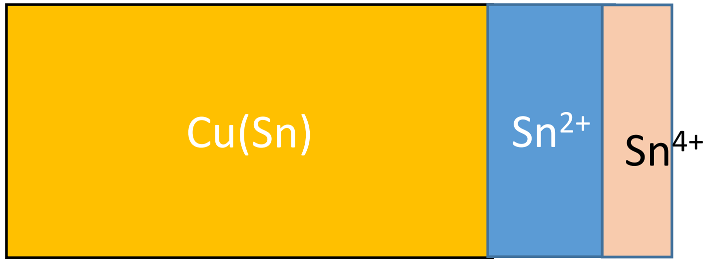
Why Electrochemical Routes?

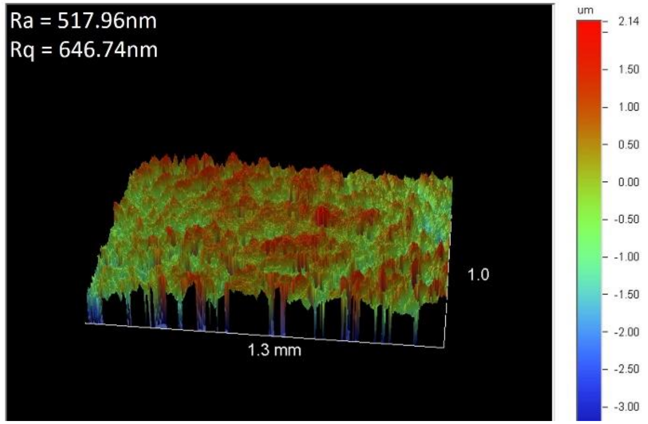
- **Advantages in process aspects**
  - conformal deposition of thin films
  - naturally purifying process
  - economical when enabled
- **Desire for bottom up approach**
  - difficulty of thin film deposition on inner surface of cavity
  - cavity with Nb3Sn layer can be produced by all thin film processes
  - polishing/repair is possible at every interface formation

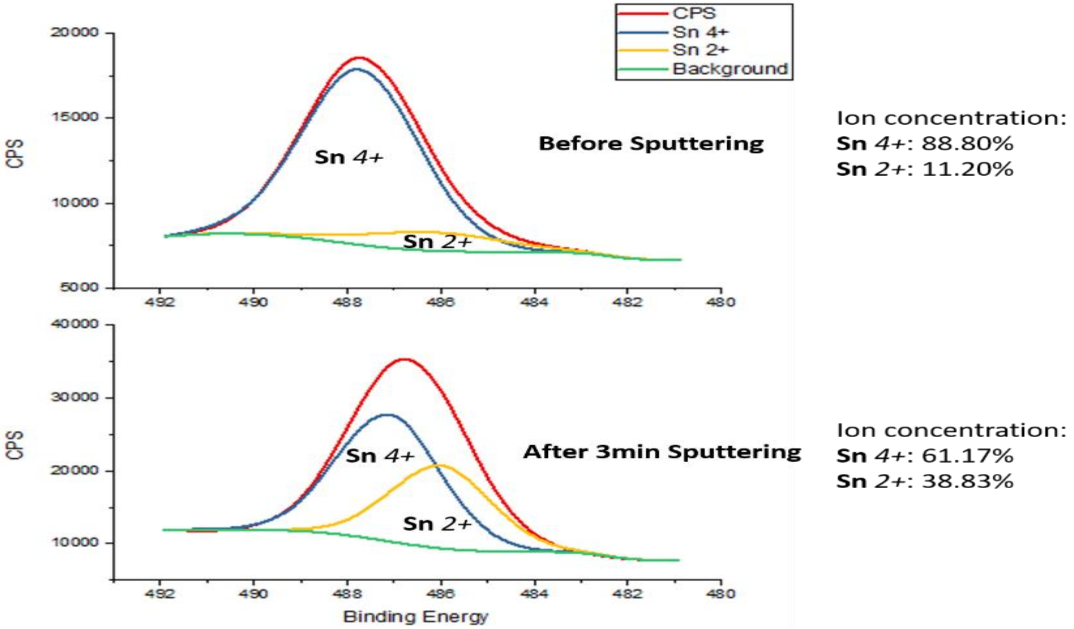


Surface Chemistry of Bronze after Electropolishing

- **EP prepared surface is not clean**
  - etching solutions react with Sn, leaving Sn^{2+} and Sn^{4+} compounds
  - the compounds interfere with Nb_3Sn reaction



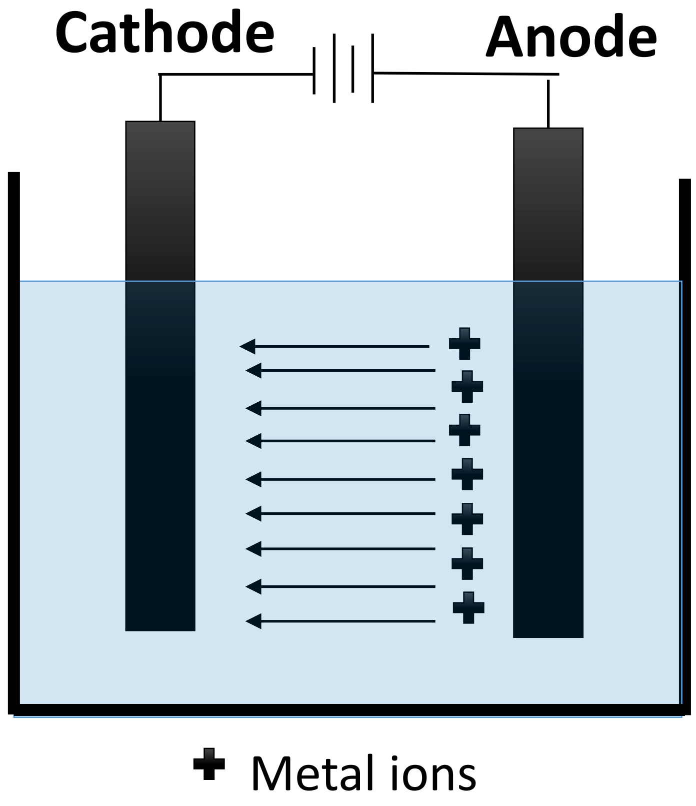




- **Bottom-up is even more desired**
  - electroplating can provide clean/flat surface of bronze
  - Cu(Sn) bronze is possible to electroplate
  - Nb can be deposited on top of bronze
  - bronze can be deposited on top of Nb

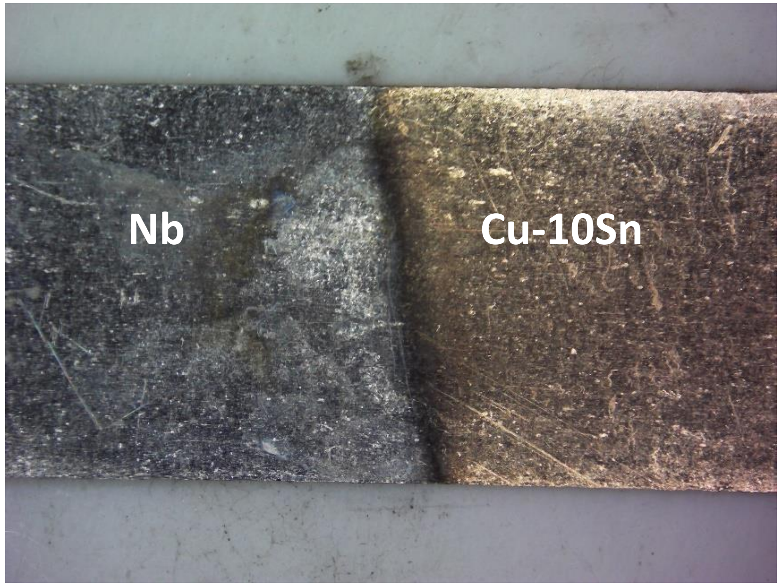
Electrochemical Deposition of Niobium and Bronze

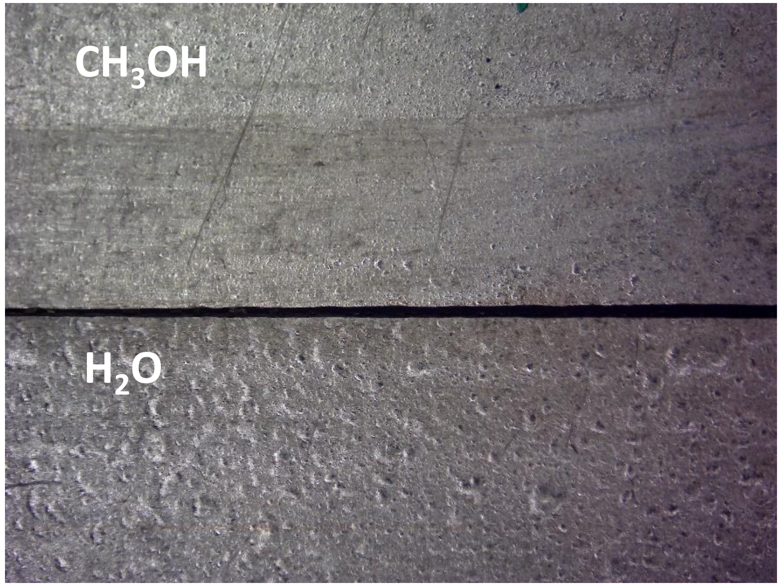
- **Electrochemical deposition**
  - rely on a simple electrochemical principle
  - overcomes limitations of PVD methods
  - conformal deposition
  - simple equipment
  - cost effective and consistent production
- **Nb plating**
  - ***no past success in plating metallic/pure Nb***
  - almost no studies on Nb electrochemistry
- **Bronze plating**
  - no prior experience on plating bronze on Nb
  - Cu/Sn composite plating has been attempted with some successes



Bronze Plating on Nb

- **Cu and Sn is electrochemically active**
  - both produces CN compounds
  - co-plating is possible in CN bath
- **Main challenges**
  - achieving/maintaining desired composition
  - removal of surface oxide of Nb
- **Two bath types for comparison**
  - Cyanide bronze plating bath (H_2O based) at 70C
  - MeOH w/ $SnCl_2$ + bronze electrode at 40C
- **Main Result**
  - H_2O: blistering when layer becomes >~0.3um
  - CH_3OH: stable film over 1um





Nb Electrochemistry Against Its Plating

- **Our studies have identified plating barriers**

  1) preferential reaction with OH- and O- in aqueous solution (Nb oxide plating not Nb)
  2) high oxidation potential; easy to be oxidized
  3) multi-valence states: disproportional reaction
  4) reactive Nb salt ($NbCl_5$, NbF_5)

- **Developed approaches**

  1) MeOH as electrolyte solution
  2) process in N2 filled environment/dehumidify MeOH
  3) pre-electrolysis treatment of electrolyte
  4) plate substate with ~50nm Au as protector

     add chemicals to remove Cl- from the solution

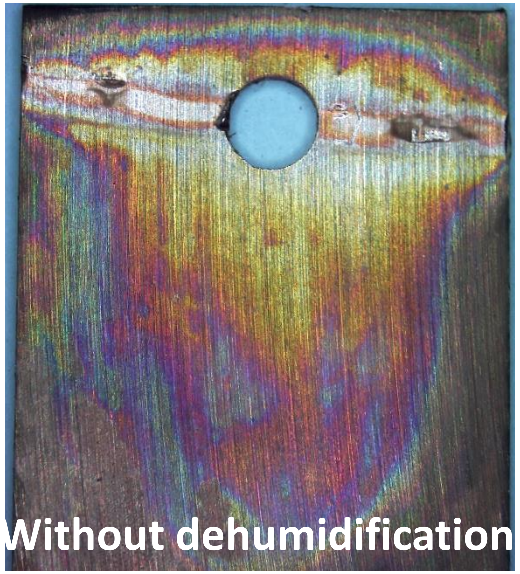
Half-Reaction	$\mathscr{E}°$ (V)
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$La^{3+} + 3e^- \rightarrow La$	−2.37

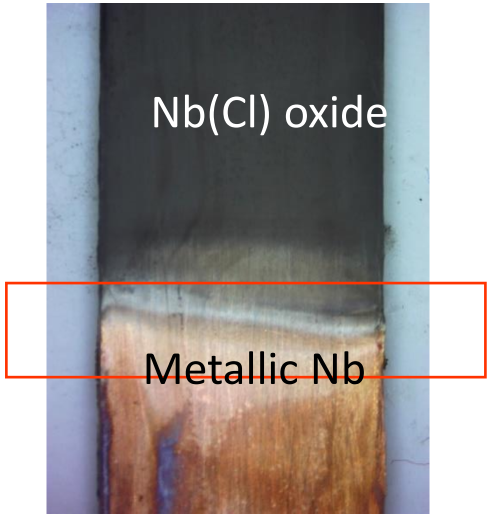
Fig 2. Standard reduction potential of metals

Key Approaches and Issues in Nb Plating

- **MeOH as electrolyte**
  - organic solvent
  - high solubility for key Nb salt ($NbCl_5$)
  - weak electrolyte: CH^{3+} , OH^-
- **Pre-electrolysis**
  - converts Nb^{5+} to Nb^{4+}
  - remove moisture : $CH_3 + H_2O = 3H_2 + CO_2$
- **Surface protection or additives**
  - main barrier against scale-up plating
  - electrolyte chemically reacts with Cu and Sn, contaminates the bath

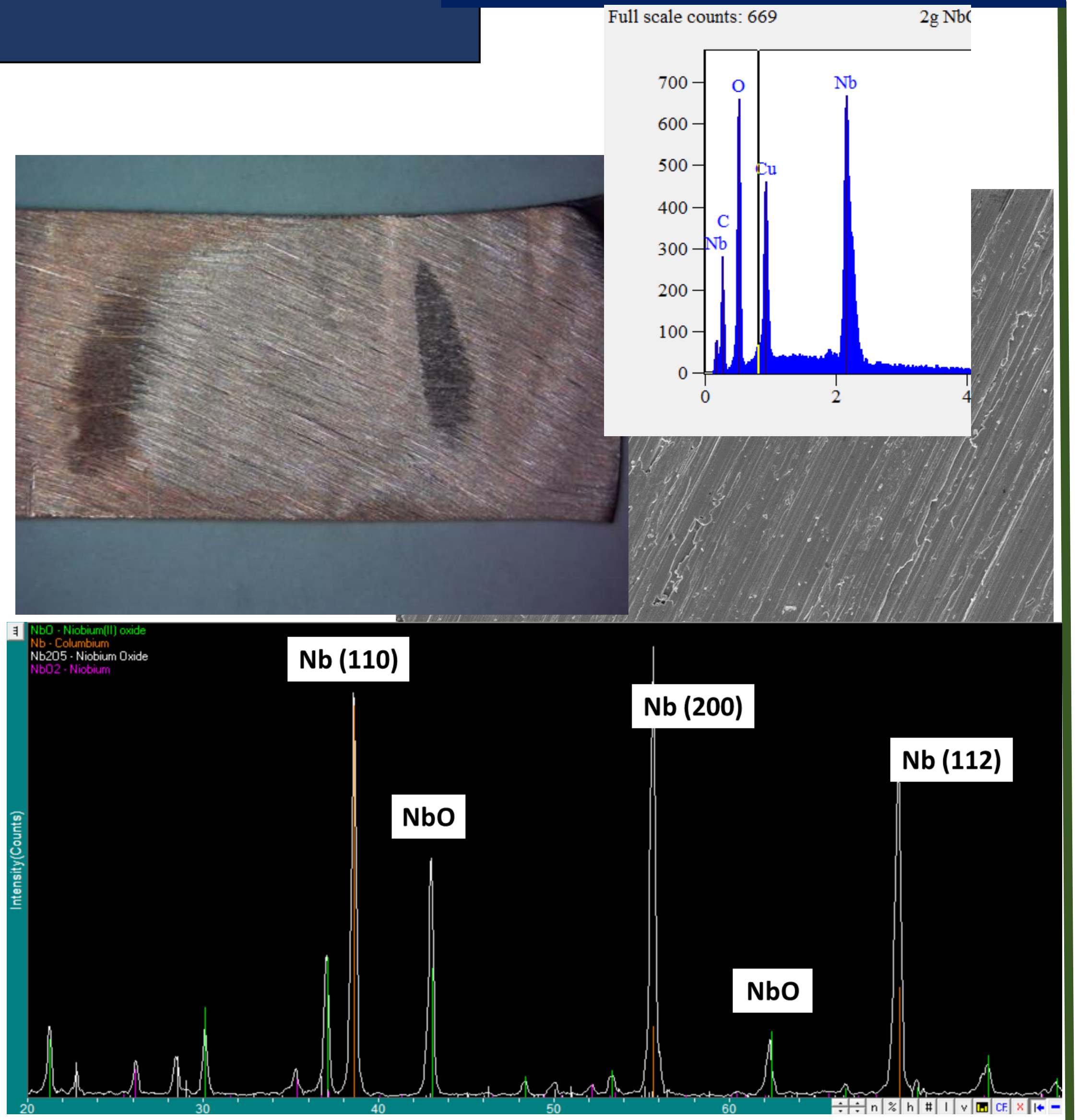
As-prepared	fully activated





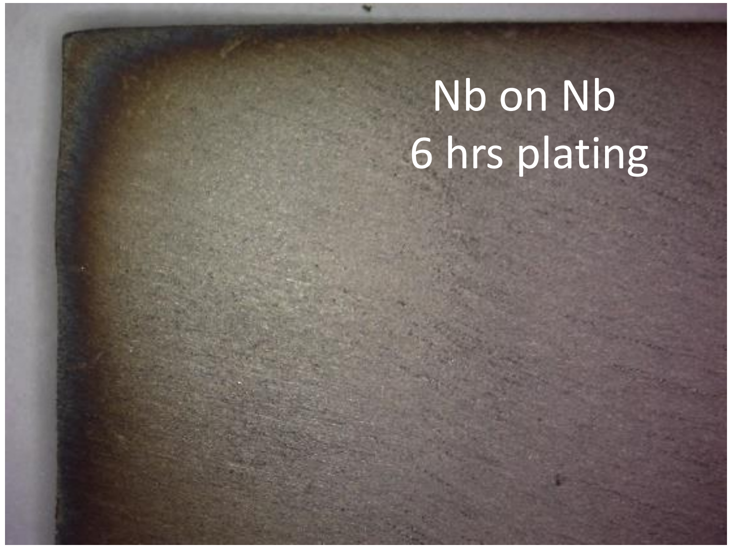
Plating Success in a Small Scale Bath

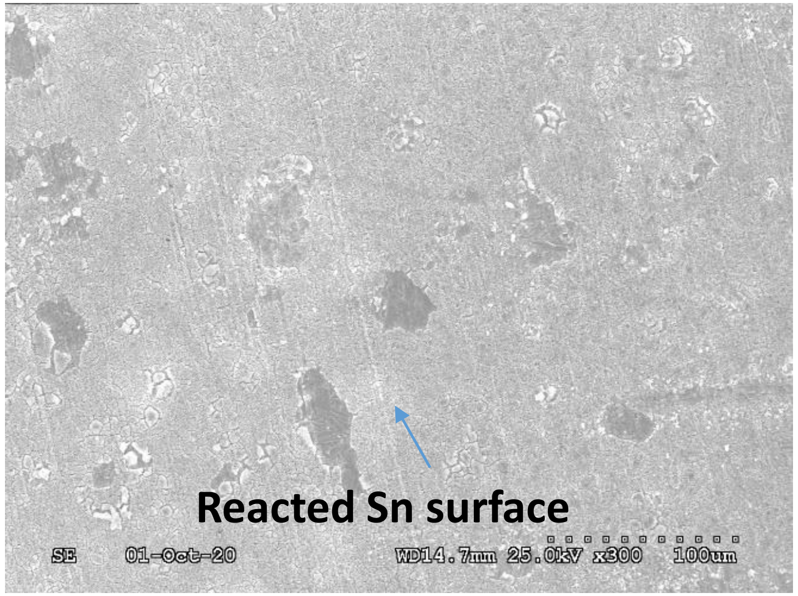
- **Metallic Nb is plated**
  - 1^{st} time in history, silvery Nb is plated
  - MeOH with $NbCl_5$ as electrolyte, Nb as Anode, Cu as cathode (others work as well).
  - weak electrolyte: CH^{3+} , OH^-
- **But, Nb quality worsens with continued plating**
  - starts to produce layer with dull texture; oxide and oxychloride layer
  - the problem worsens when electrolyte is more
  - major obstacle against scale-up plating

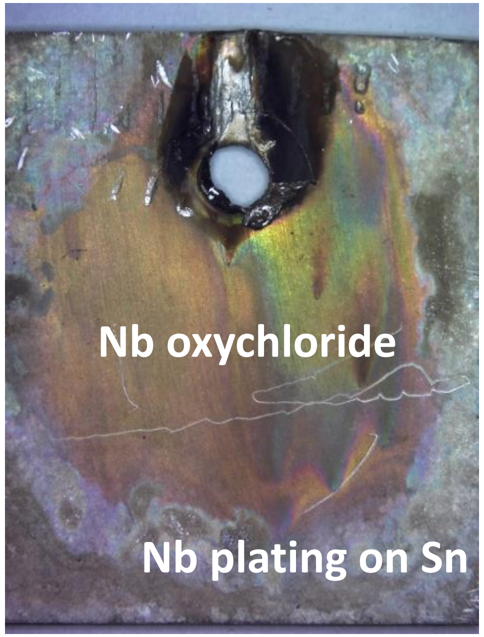


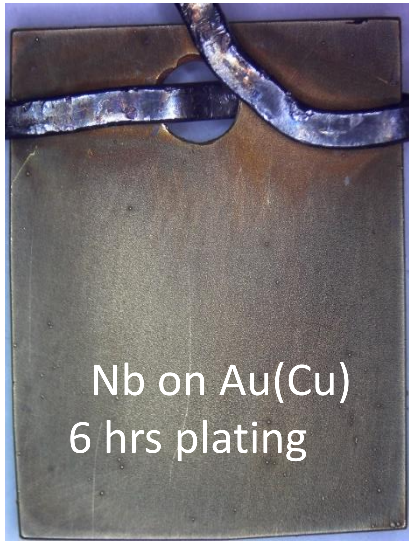
Contamination: Barrier Against Scale-up Plating of Pure Nb

- **The electrolyte fouling is found to be linked to contamination from the substrate**
  - plating in small amount of electrolyte works well
  - Nb plating on Nb works even in large bath
  - Au coating before Nb coating substantially extends the life of electrolyte



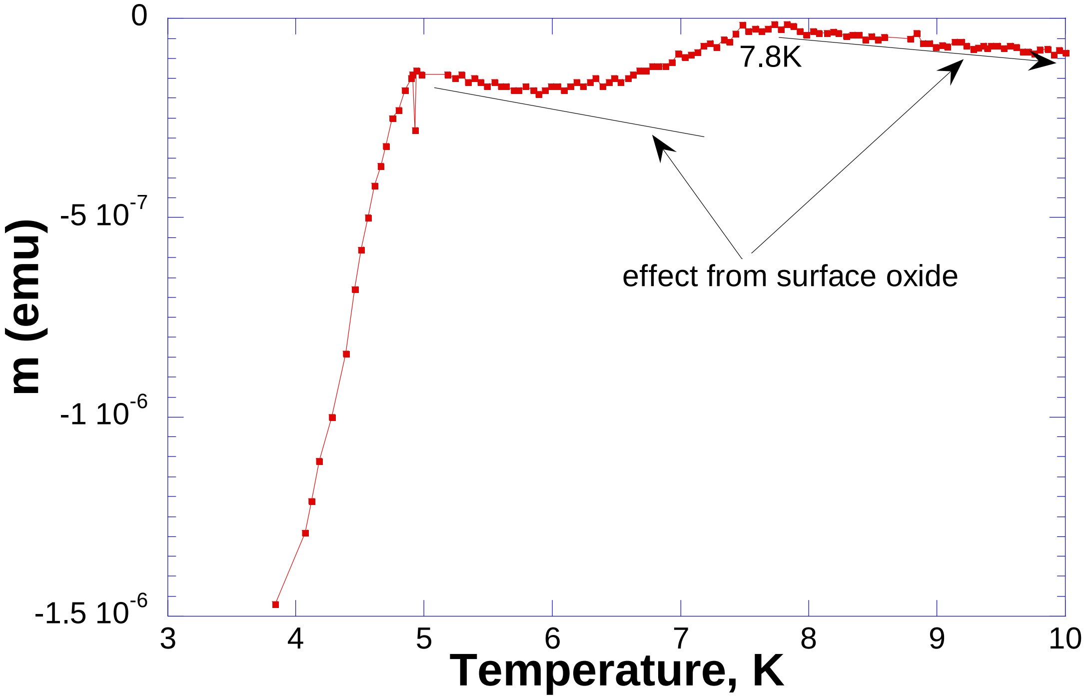


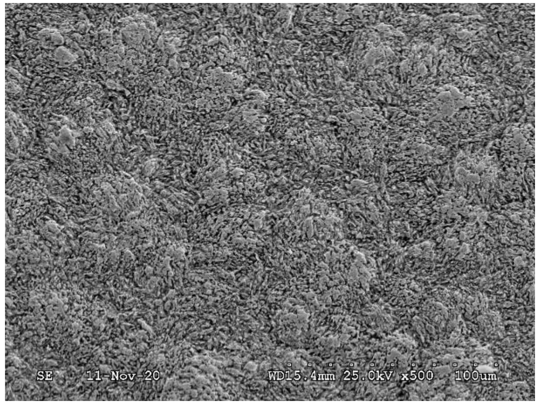




Evidence of Superconductivity from Electroplated Nb

- **Thin Nb plated on Au/bronze**
  - Au is to protect bronze surface
  - Nb_3Au's property is similar to Nb_3Sn
  - ~50nm Au may be practical and produces $Nb_3(Sn,Au)$ superconductor
- **T_c~7.4K**
  - reduced from 9.2K probably due to 1) thinness of film and 2) surface oxide
  - upward slopes in *m* may indicates surface oxide ($Nb_{12}O_{29}$)
  - transition at 5.4K may also be related to oxide
  - oxide effect will be reduced and eliminated in thick Nb





Trial of Bottom-up Process

- **Partial but important success**
  - key processes are tried staring from wax model to Nb (~3” tall)
  - cracks and uneven coating are seen due to improper handling of the sample; optimization is in progress

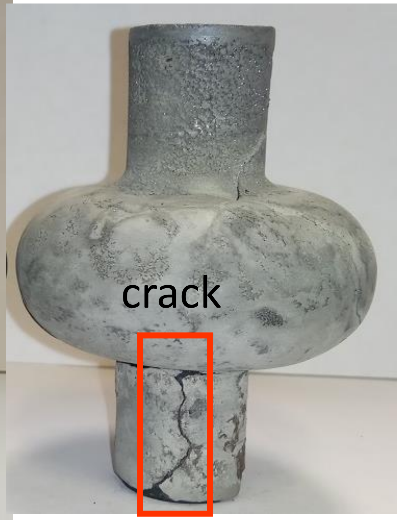
Wax sample

Conductive layer painting

Cu electroplating for strength

Cu polishing

Au/Bronze



Nb

Optimization Needs: Stress

- **Cracking in the plated layers**
  - needs thicker inner Cu to provide sufficient strength until completion of all coatings (then remove)
  - easy problem to solve

- **Surface roughing with thick coating**
  - nature and can be minimized
  - polishing can be conducted

- **CTE driven delamination during reaction inducing process**
  - needs to adjust bronze layer/Nb thickness ratio
  - may need to use buffer layer
    (crack shown here probably formed during heating ramp)

Conclusion and Future Work

- **Electroplating processes for bronze route is more than feasible**
  - metallic and pure Nb can be plated on Cu and bronze
  - thin Au layer may make Nb/bronze process more practical with Au protecting electrolyte
  - mechanisms behind past challenges in electroplating processes are well understood to the level to try the “bottom-up” construction of SRF.

- **Future Work**
  - continue with process optimizations
  - produce well processed model SRF entirely made by electroplating process, staring from the wax to the electroformed Cu.

Acknowledgement

- DOE Funding (*DE-SC0018379)*
- Collaborators
  - at FSU/National High Magnetic Field Laboratory
  - at Baileytools
  - at UT Arlington: PhD Students