Nb_3Sn Formation Using Electroplating Method for SRF Cavity

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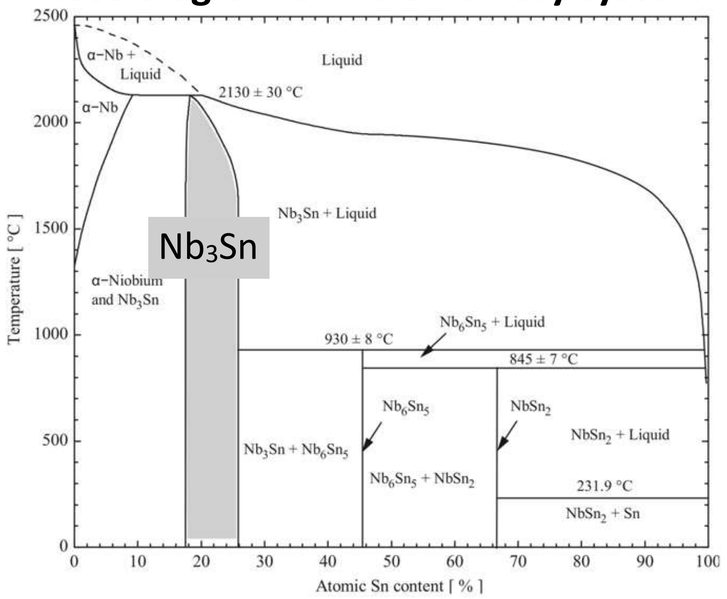
Outline

- What advantage of electroplating method for the Nb_3Sn cavity
- Electroplating process at KEK
- Forming the Nb_3Sn layer
- Removing the bronze layer remained after heat treatment
- SEM observation and T_c measurement results
- Summary

Nb_3Sn forming process

Center for Applied Superconducting Accelerator 応用超伝導加速器センター

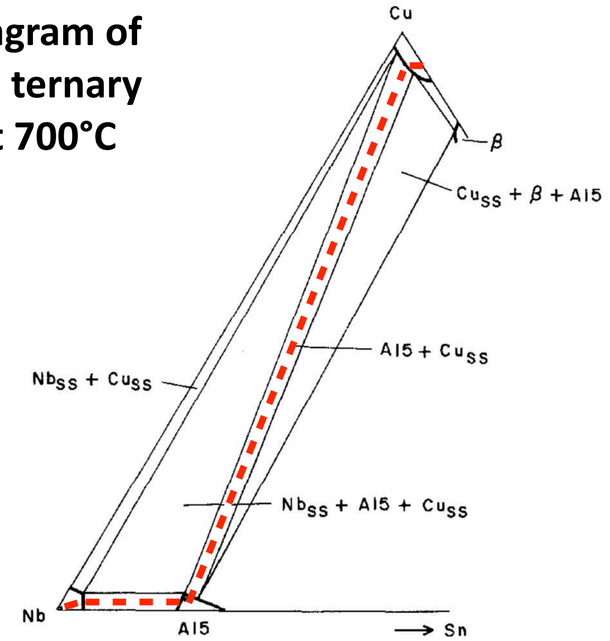
Phase diagram of Nb-Sn binary system



A. Godeke, Superconductor Science and Technology, 19(8):R68–R80, jun 2006.

In the vapor diffusion method, we require a temperature of above **~ 1000°C** to form Nb_3Sn stably.

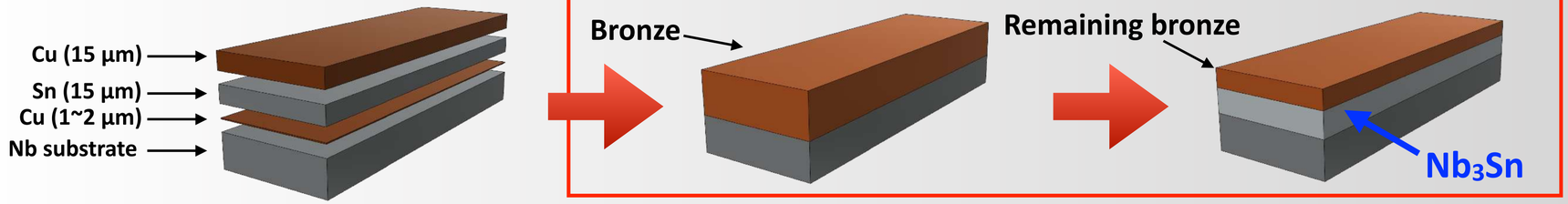
Phase diagram of Nb-Cu-Sn ternary system at 700°C



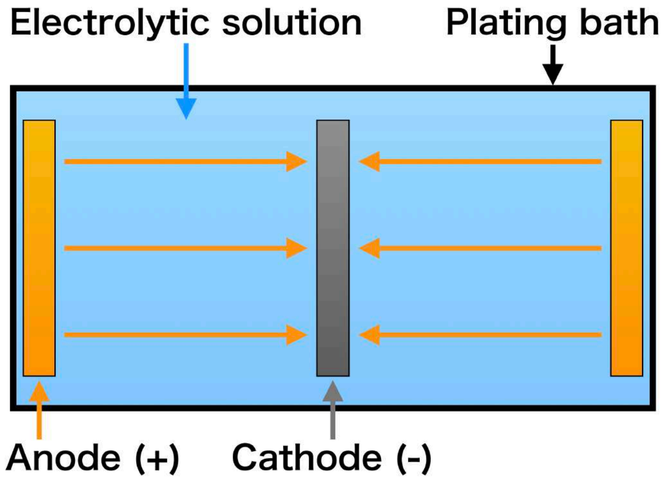
D. Dew-Hughes and T. S. Luhman, Journal of Materials Science, 13(9):1868-1876, Sep 1978.

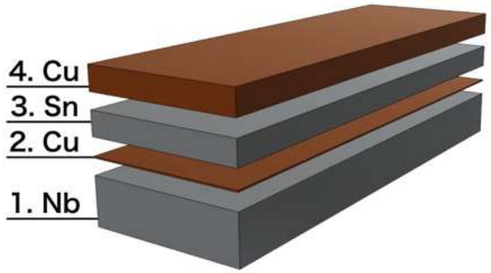
We can obtain the Nb_3Sn phase at **700°C** by the bronze route.

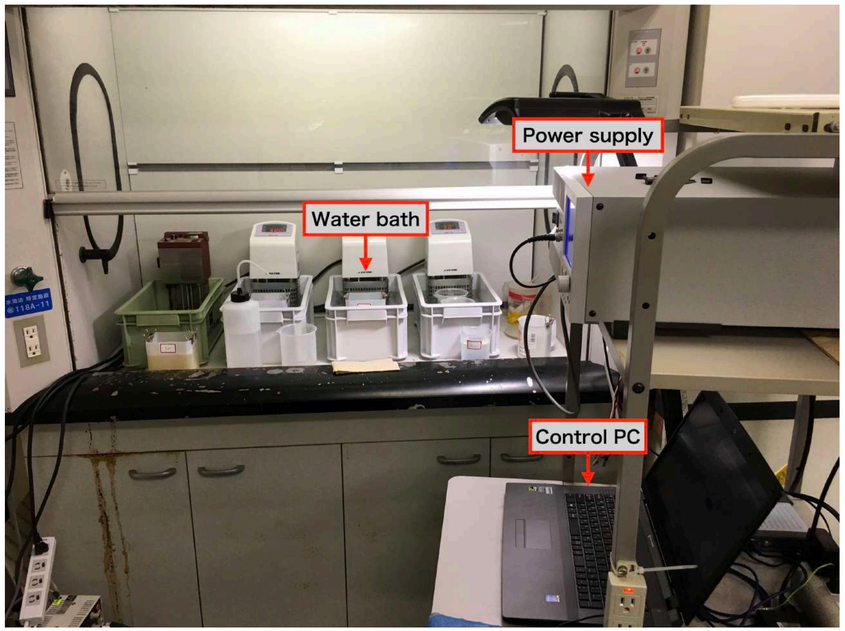
Electroplating method for forming the Nb_3Sn layer



Electroplating process

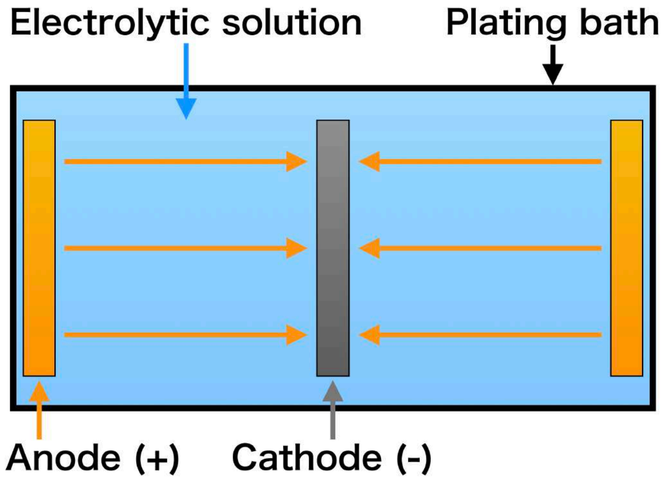


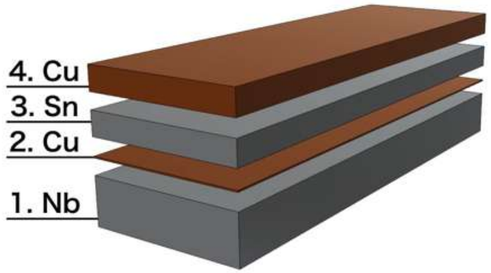




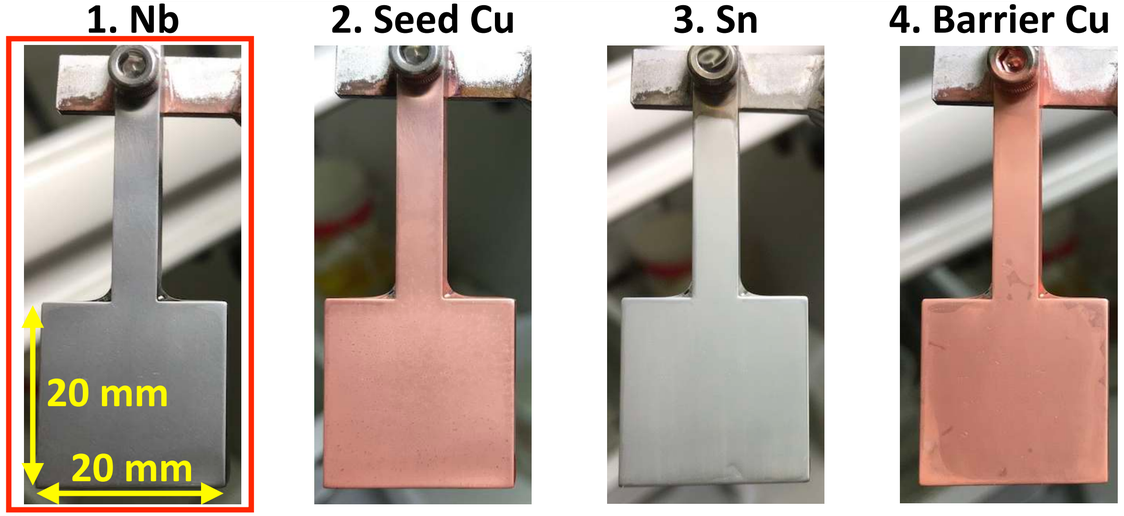
Process	Chemicals	Concentration [/L]
Alkaline degreasing	Ace Clean 801	50 g
↓ Rinsing		
Electrolytic degreasing	NaOH	50 g
	Top Cleaner E	50 ml
↓ Rinsing		
Etching	Etchant TI	100 ml
↓ Rinsing		
Desmut	35%-HCl	100 ml
↓ Rinsing		
Strike copper plating	Top Soft Copper M	500 ml
	Top Soft Copper 3	20 ml
	Top Soft Copper S	50 g
↓ Rinsing		
Acidic tin plating	Stannous Sulfate	30 g
	98%-H_2SO_4	185 g
	Top Floona Mu	20 ml
	Top Floona R	8 ml
↓ Rinsing		
Copper pyrophosphate plating	RAIKI Copper pyrophosphate solution	200 ml

Electroplating process





Plating results for TD's Nb



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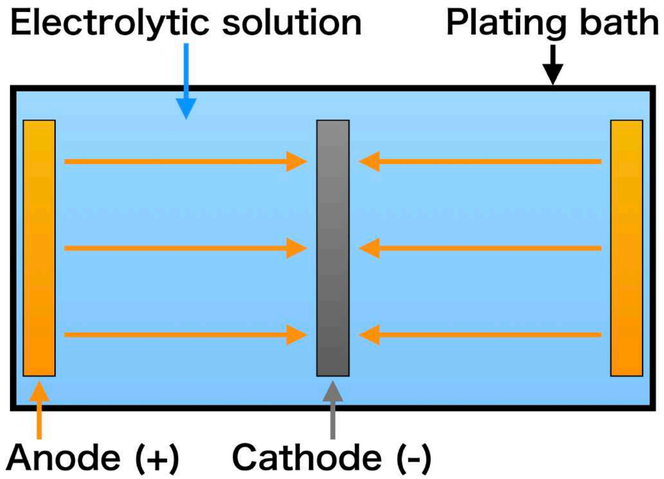
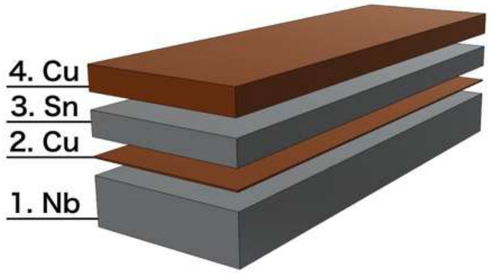
	Top Floona Mu	20 ml
	Top Floona R	8 ml
↓ Rinsing		
Copper pyrophosphate plating	RAIKI Copper pyrophosphate solution	200 ml

Pre-treatment for plating

Electroplating process





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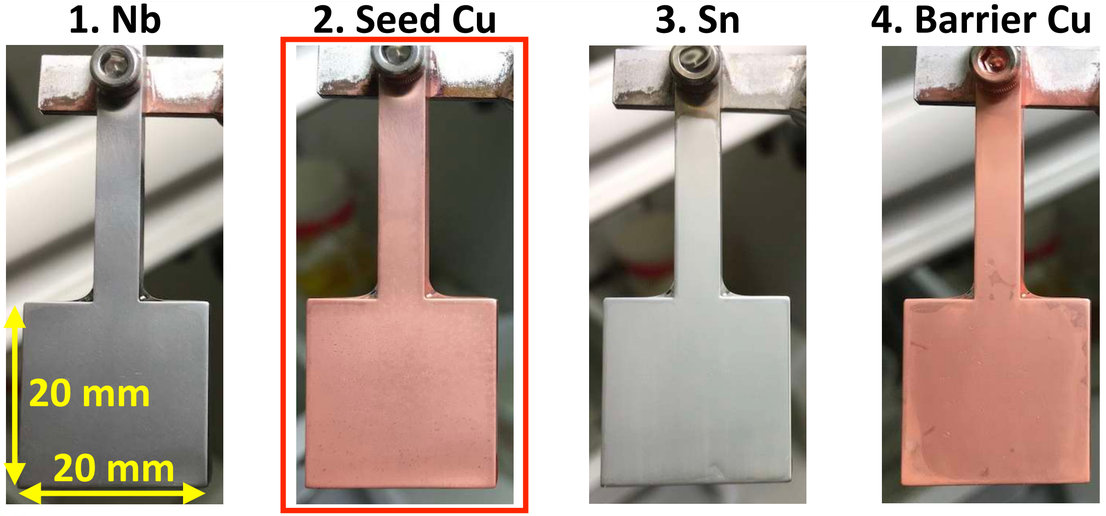

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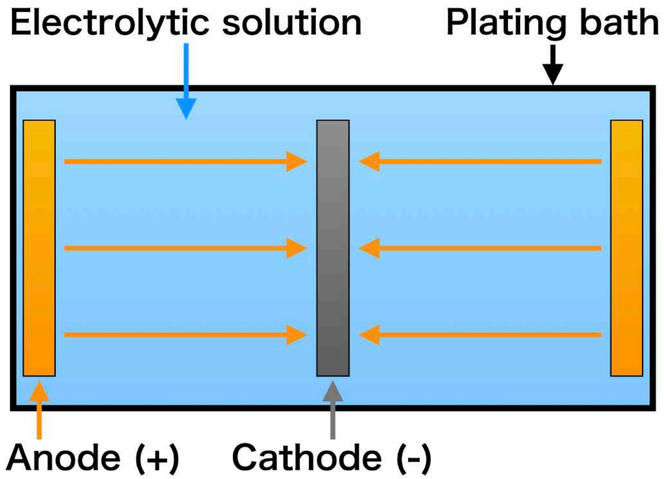
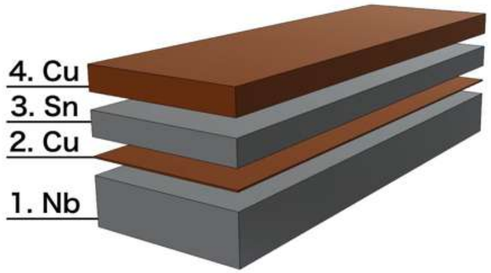
	Top Floona Mu	20 ml
	Top Floona R	8 ml
↓ Rinsing		
Copper pyrophosphate plating	RAIKI Copper pyrophosphate solution	200 ml

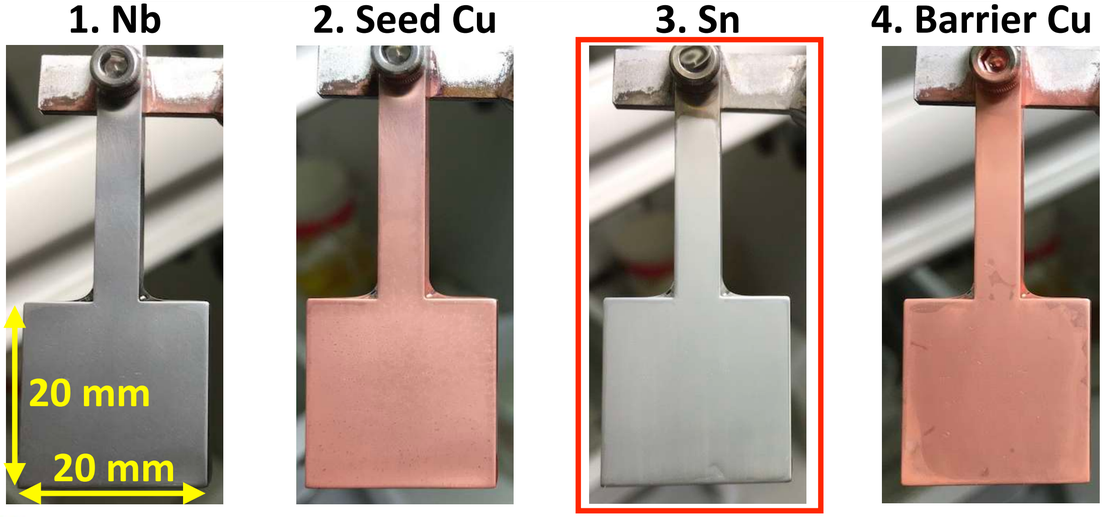
2. Seed Cu plating

Electroplating process





Plating results for TD's Nb



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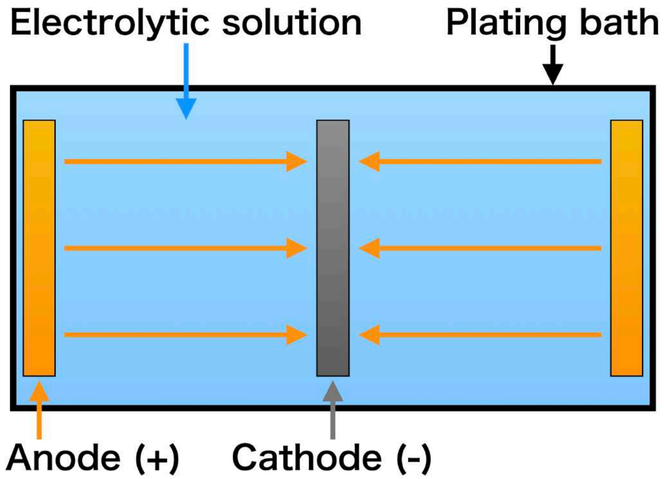
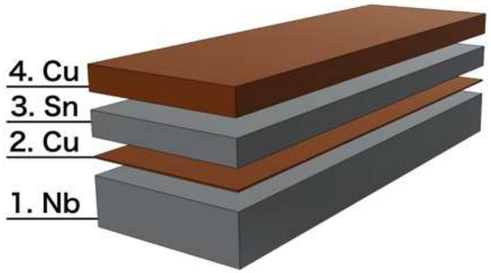
	98%-H_2SO_4	185 g
	Top Floona Mu	20 ml
	Top Floona R	8 ml
↓ Rinsing		
Copper pyrophosphate plating	RAIKI Copper pyrophosphate solution	200 ml

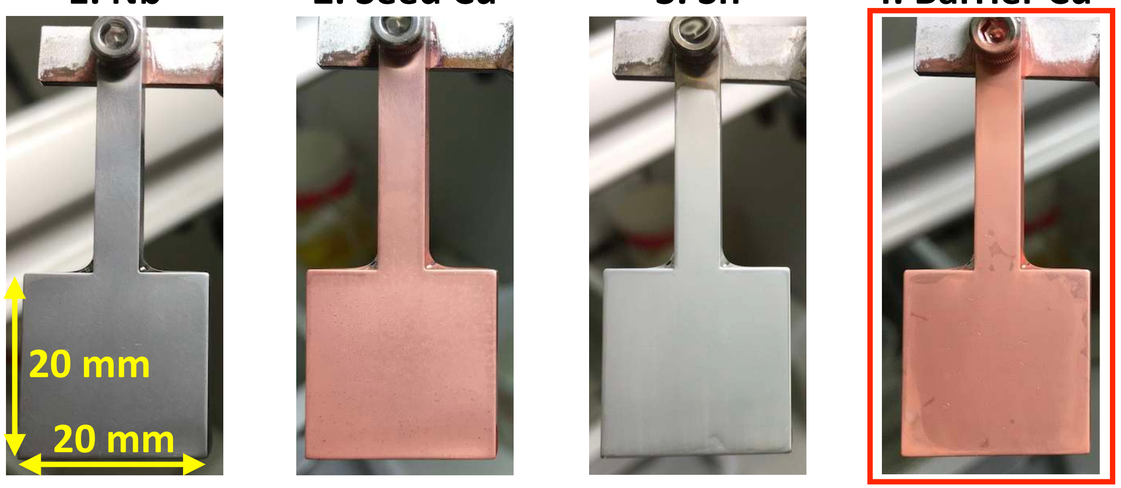
3. Sn plating

Electroplating process





Plating results for TD's Nb



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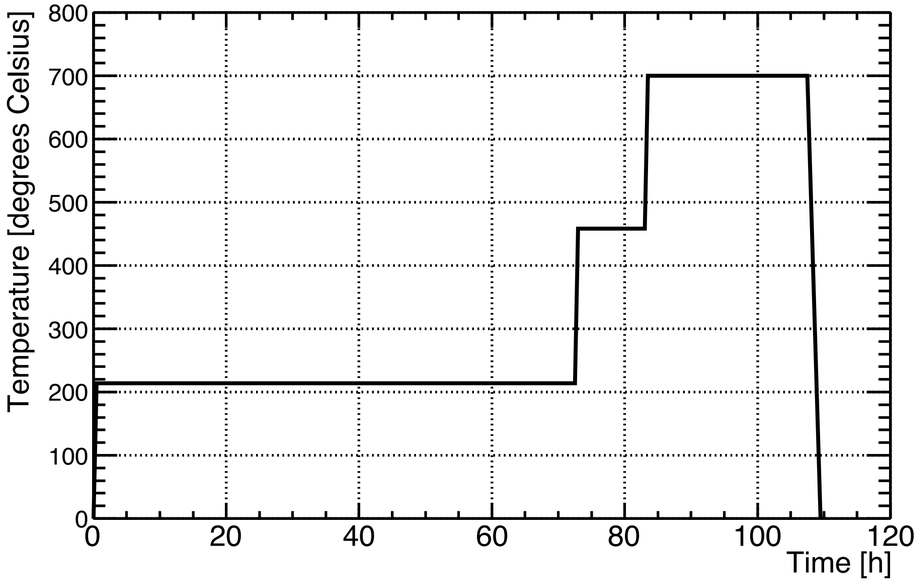
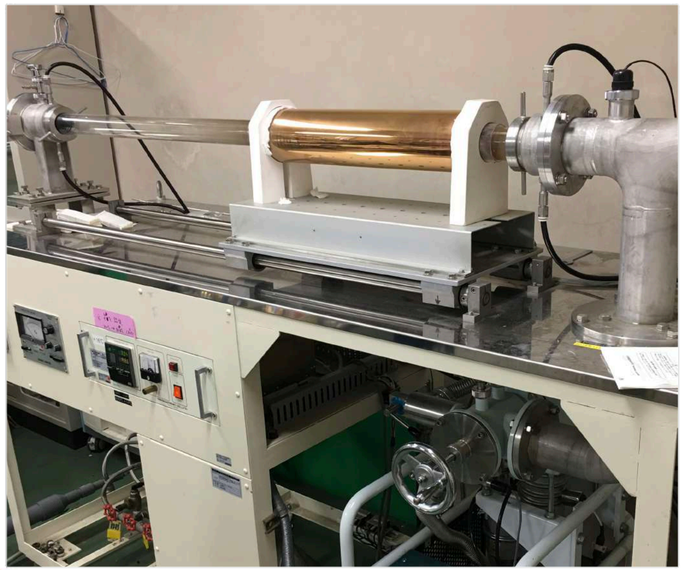
	98%-H_2SO_4	185 g
	Top Floona Mu	20 ml
		8 ml
↓ Rinsing		
Copper pyrophosphate plating	RAIKI Copper pyrophosphate solution	200 ml

4. Barrier Cu plating

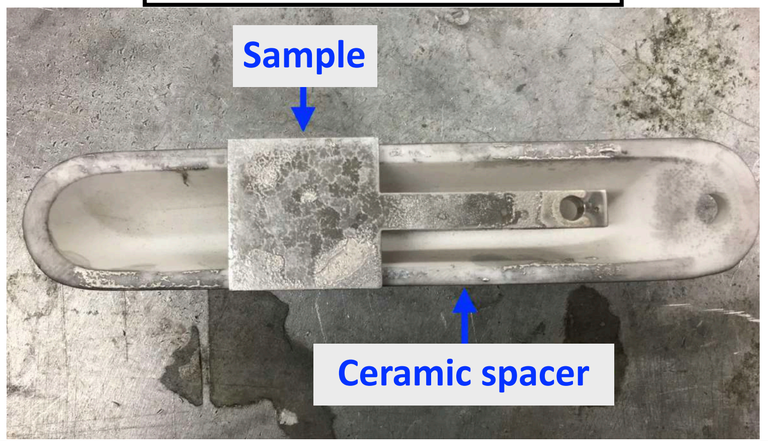
Heat treatment to form Nb_3Sn





- **214°C for 72 h**
  ->Relieve the stress on the plating layer.
  The diffusion reaction between Sn and Cu starts.
- **458°C for 10 h**
  ->The Sn layer is liquefied.
  The diffusion reaction between Nb and Cu starts.
- **700°C for 24 h**
  ->Nb_3Sn layer is formed.

After Heat treatment



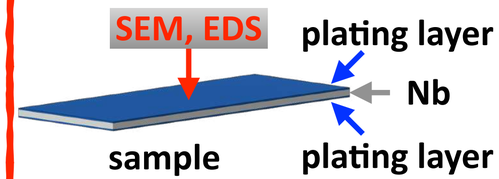
The bronze layer remained on the sample surface.

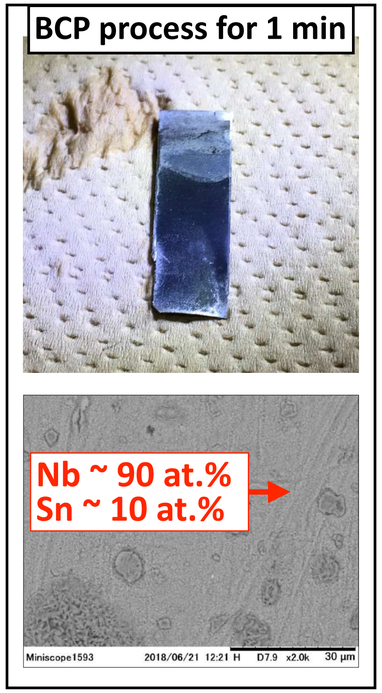
Removing bronze layer

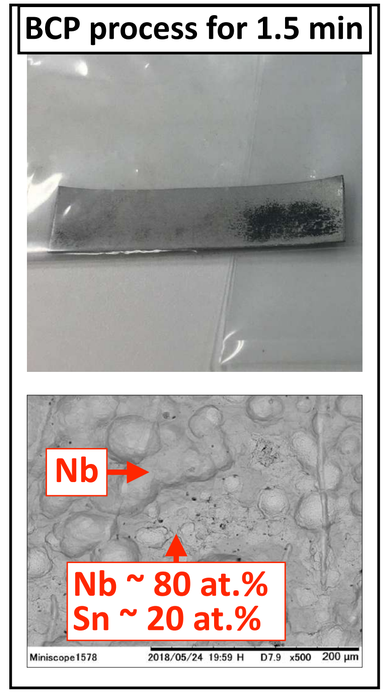
Chemical Solution	Reactivity
HNO_3: H_2O = 1: 1	No
HNO_3: H_2O = 30: 5 (at 60°C)	No
HCl	No
HCl: H_2O_2 = 1: 1	No
BCP (HNO_3: HF: H_3PO_4 = 1: 1: 1)	O.K.
Aqua regia (HCl: HNO_3 = 3: 1)	O.K.

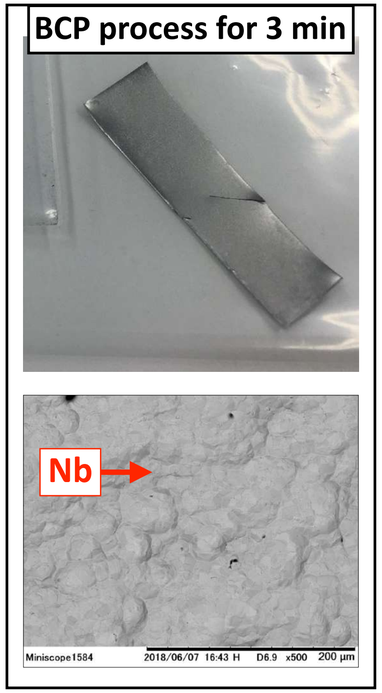
BCP treatment

We attempted to remove the bronze layer using BCP liquid (HNO_3: HF: H_3PO_4 = 1: 1: 1) for FNAL's samples.



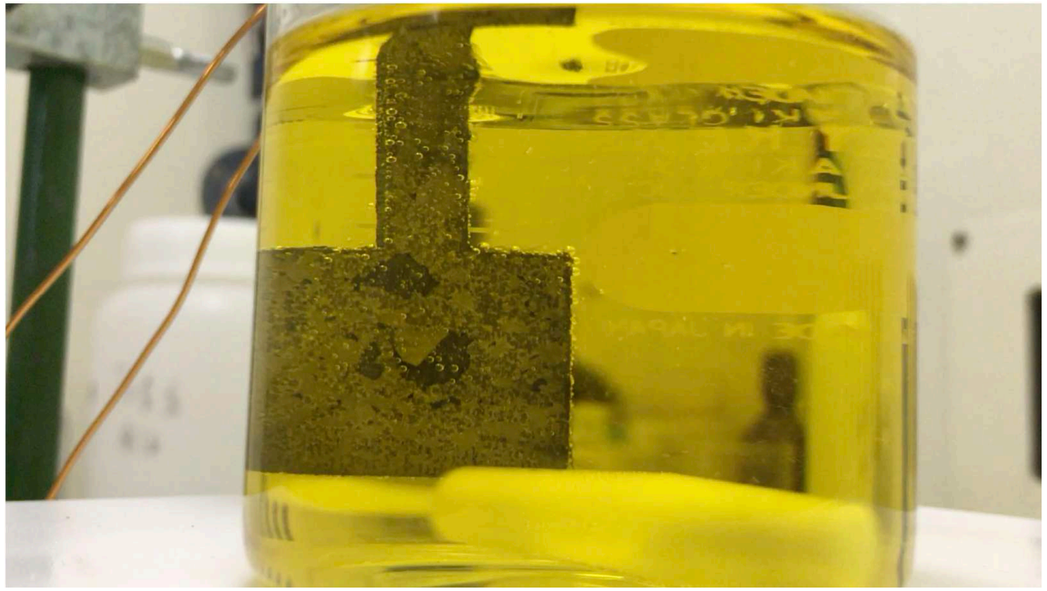






The bronze layer was removed using the BCP solution as well as the Nb_3Sn layer.

Aqua regia treatment



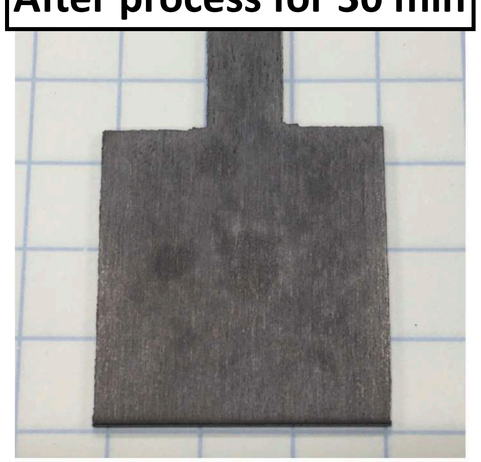
Aqua regia (HCl: HNO_3 = 3: 1) treatment was applied to KEK's samples.

Processing time	Sample weight
0.5 h	4.5357 g
1 h	4.5355 g
3 h	4.5355 g

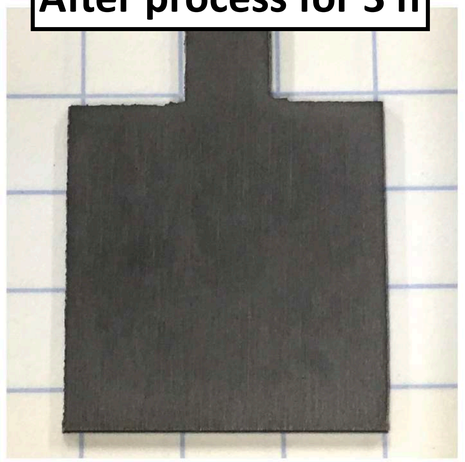
The bronze layer was removed by aqua regia treatment process for 30 min.

KEK's sample

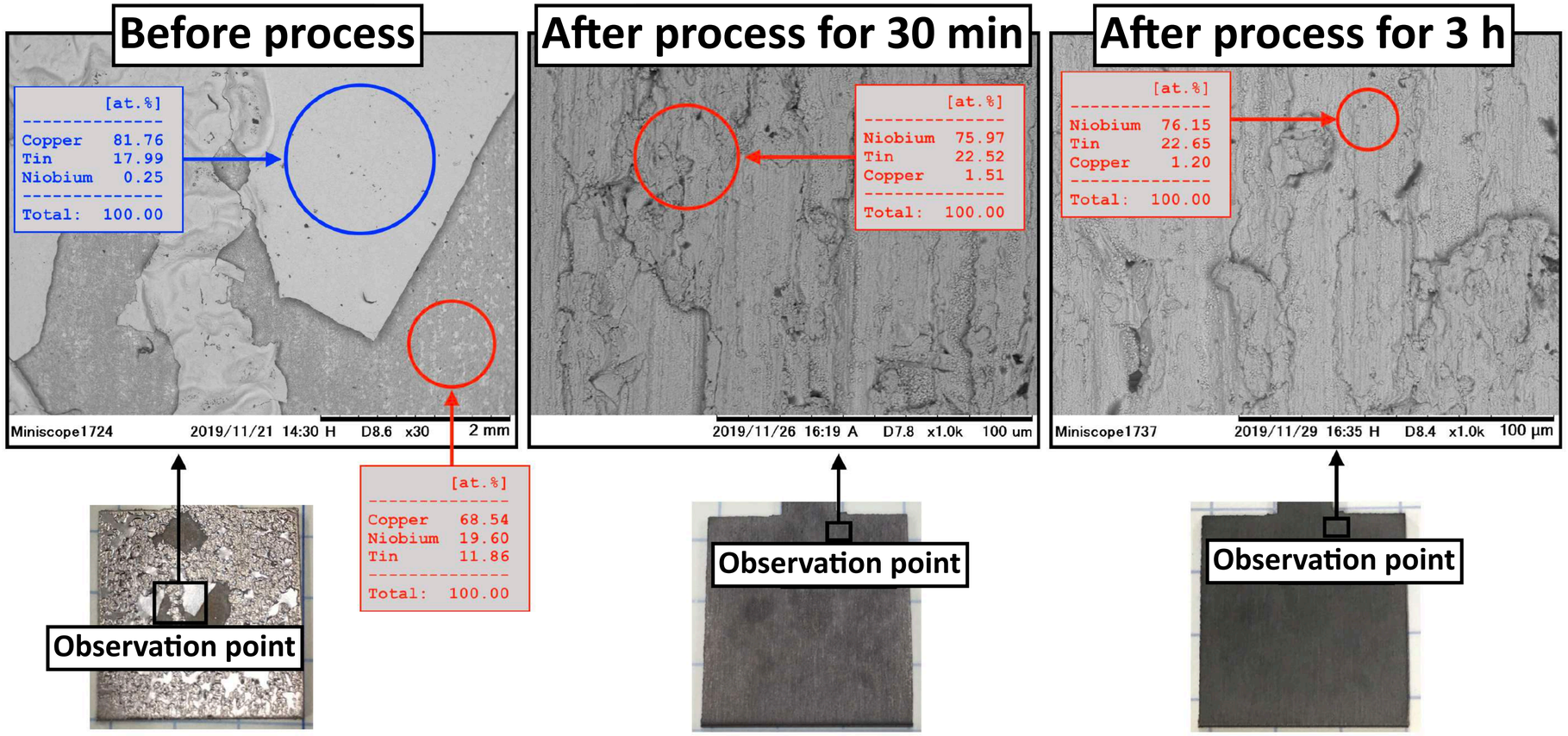
After process for 30 min



After process for 3 h

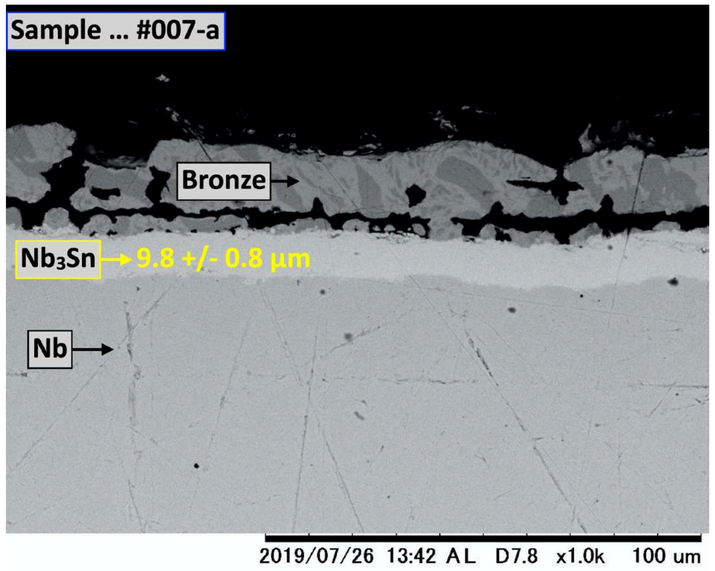


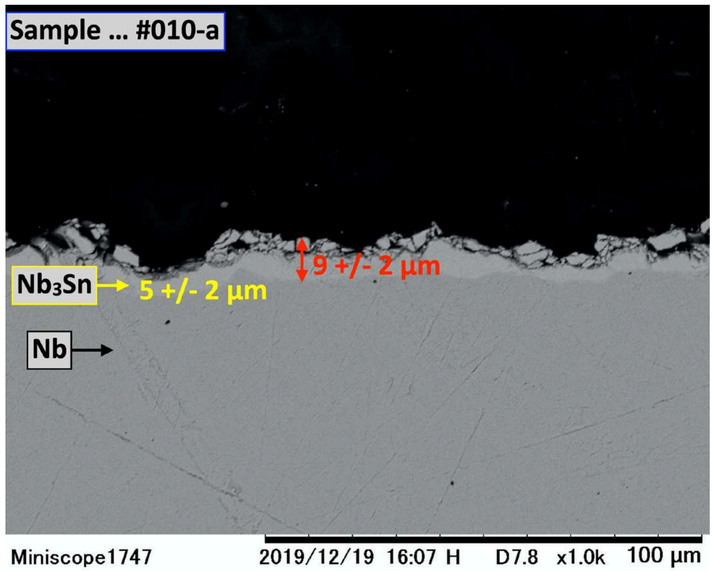
Aqua regia treatment



There was no change in the weight of the samples after over 1 h of treatment with aqua regia and no change in the appearance of the Nb_3Sn surface by SEM observation.
-> Nb_3Sn is stable to aqua regia at room temperature.
-> Only the bronze layer could be removed by aqua regia treatment.

SEM observation



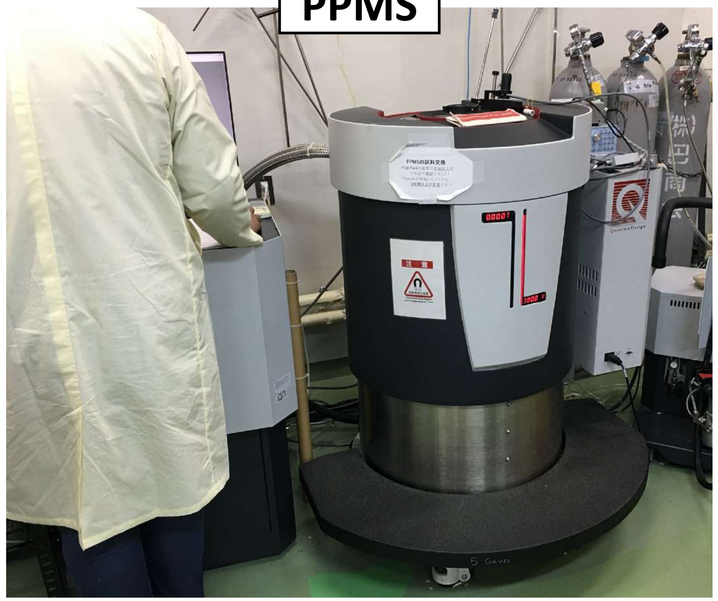


Sample No.	Nb substarate	Nb_3Sn layer	Note
007a	Nilaco	9.8 +/- 0.8 µm	
010a	Nilaco	5 +/- 2 µm (9 +/- 2 µm)	Bronze layer is removed
014a	Nilaco	11 +/- 2 µm	
016a	Nilaco	11 +/- 1 µm	
018b	TD	10.7 +/- 0.9 µm	

- **The Nb_3Sn layer is around 10 µm thick in the sample before removing the bronze layer**
- **After the removal process, the thickness is 5 µm (9 µm if the fragment on the surface is taken into account)**
  -> The Nb_3Sn phase might not be formed at upper side of the Nb_3Sn layer

T_c Measurement

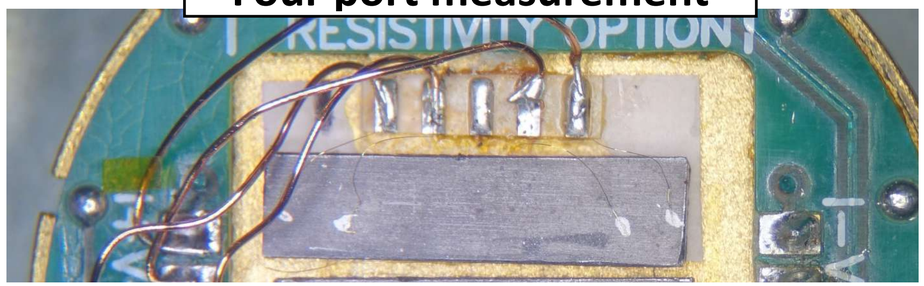
PPMS

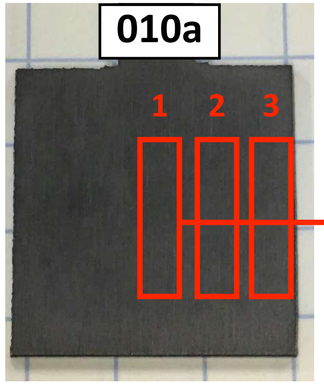


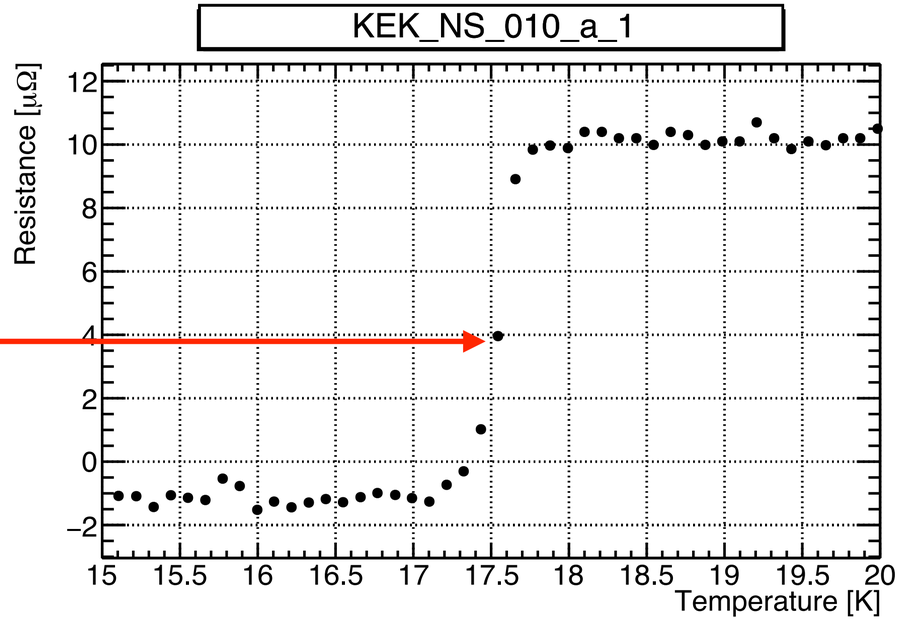
For each of the four samples, strips of 3 mm*11 mm were cut out and numbered 1, 2, and 3 from the center, as shown in the red box.

Four samples were measured, 010a, 014a, 016a, and 018b, for a total of 12 T_c measurements.

Four port measurement





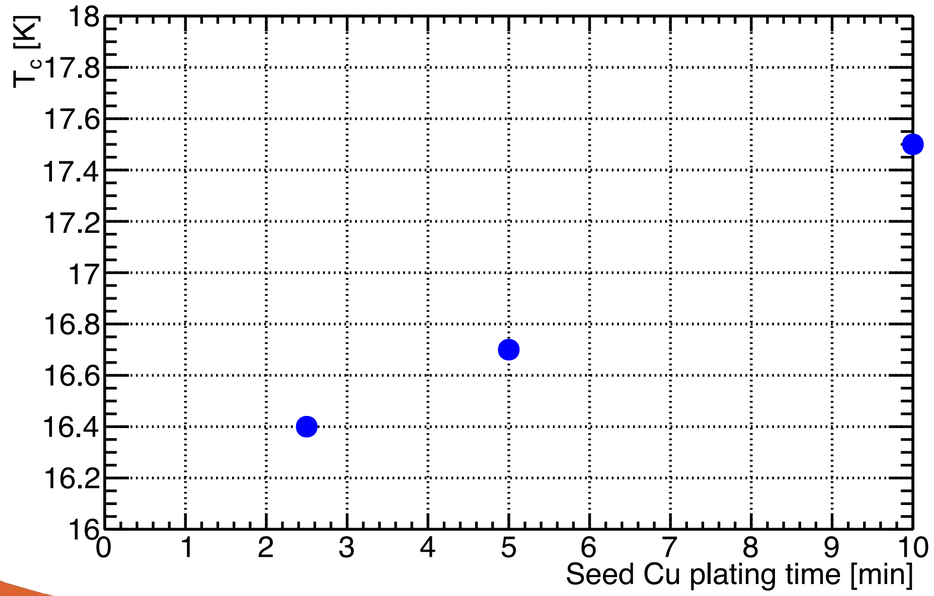


All the measured samples superconducting transitioned.

T_c Measurement

Cutout position

Sample No.	Nb substrate	Seed Cu		Sn		Brrier Cu		①		②		③		
		J	time	J	time	J	time	Tc	width	Tc	width	Tc	width	Average
010a	Nilaco	2 A/dm^2	**10 min**	4 A/dm^2	7.5 min	4 A/dm^2	15 min	17.5	0.32	17.5	0.43	17.5	0.45	**17.5**
014a	Nilaco	2 A/dm^2	2.5 min	4 A/dm^2	20 min	4 A/dm^2	15 min	17.1	0.81	17.4	0.43	17.5	0.35	17.3
016a	Nilaco	2 A/dm^2	**5 min**	4 A/dm^2	7.5 min	4 A/dm^2	10 min	16.5	1.2	16.7	1.4	17	1.1	**16.7**
018b	TD	2 A/dm^2	**2.5 min**	4 A/dm^2	7.5 min	4 A/dm^2	10 min	16.7	1	16.5	1.3	16	0.73	**16.4**



- The thicker the seed Cu layer, the higher the T_c tends to be. Also, the variation of T_c at each position tends to be small
- The transition was observed in the 010a sample which was immersed in aqua regia for 3 hrs to remove the bronze layer

  -> Deterioration of Nb_3Sn by the aqua regia process is not expected

Summary

- We focused on the bronze route which is widely used in the superconducting wire and performed a test of Nb_3Sn formation using the electroplating method
- Each Cu and Sn layers were plated successfully and uniformly
- Only the bronze layer was successfully removed in the removal test with aqua regia
- The Nb_3Sn layer with a thickness of around 10 µm was confirmed by SEM cross-sectional observation
- A T_c measurement using PPMS confirmed a transition temperature of 17.5 K for KEK's sample
- We are planning to test the formation of Nb_3Sn film on a larger area of Nb plates and cylindrical Nb plates