PHY905 Section 4
Ion Accelerator Technology
Lecture 6
- High Purity Niobium Industrial Production -

Yoshishige Yamazaki, Kenji Saito, Steve Lidia
National Superconducting Cyclotron and Facility for Rare Isotope Laboratory
Michigan State University

High Purity Niobium Industrial Production

6.1 Niobium information

6.2 Niobium ore and refining

6.3 Industrial high purity Niobium sheet production

6.4 Quality control

6.5 Advanced sheet production for large grain cavities

6.6 Approach for single crystal ingot

6.1 Information of Niobium

- 35000 ton Nb_2O_5 can produce, 2450 ton niobium metal in 2000
- The demand is increasing by15 – 20% /year
- Niobium deposit is over the amount of 500 year's needs
- 90% of the total consumption of niobium is Ferro niobium for iron alloy
- Two kinds of niobium ore: Pyrochrore and Columbite
- Pyrochore (top three mines) contains 2.5 – 3% of Nb_2O_5 in average.
- Columbite includes both niobium ore and tantalum ore, which needs a special chemical isolation refining method
- Price of the niobium metal in the Ferro niobium is $15 US/kg
- Price of the standard niobium ingot (250mm Dia x 1.5 m long, 3 times EBW melted) is ~ $55 US/kg in 2000. Now it will be expensive by a factor 1.5.

Niobium needs

- Niobium metal
  - Pure niobium metal
    - Ingot
    - Sheets, foils
    - Bars, wires
    - Grain, stuff to principle forms
  - Pure niobium metal
    - Nb-Zr alloys
    - Biometal Nb alloy
    - Thermostable Nb super alloy
    - Electronic Nb alloy material
  - Intermetallic compounds
    - Superconductors: Nb_3Sn, Nb_3Al, NbTi
    - Ultrahigh temperature Nb_3TNi
    - Hydrogen absorption NbTi
    - Shape memory alloy NbTi
- Additive to other metals
  - Ferro niobium for steel
  - Vacuum-Gr Ferro niobium
  - Nickle-niobium
- Niobium oxide
  - Common Nb_2O_5
  - Nb_2O_5 additive to optical lenses
  - Catalyzer
- Others niobium compounds
  - Niobium fluorides, niobium chlorides
  - Alkali-Nb metal complex
  - Others (Ammonium salt complexes)

6.2 Niobium ore and refining

Niobium Ore: Pyrochlore, Columbite

Top three mines of Niobium ore in the world
Brazil :Araxa; Catalao.
Canada: St. Honore

Niobium is 33rd position with enriched metal elements on the Earth.

Example: CBMM (company) in Araxa, Brazil

CBMM Niobium mine

Araxa in Brazil

60 hr travel from East Lansing.

Niobium material production process

Nb ores

↓

Crushing (powder)

↓

Floatation (includes magnetic concentration)

↓

Washing (Concentration of Nb_2O_5), Acid Leaching method, Electric furnace dissolution

↙ ↘

for Other Nb except Ferro Nb

↓

High purity Nb_2O_5

↓

ATR (a kind of TERMIT method)

↓

EB melting

↓

Nb ingot

for Ferro Nb

↓

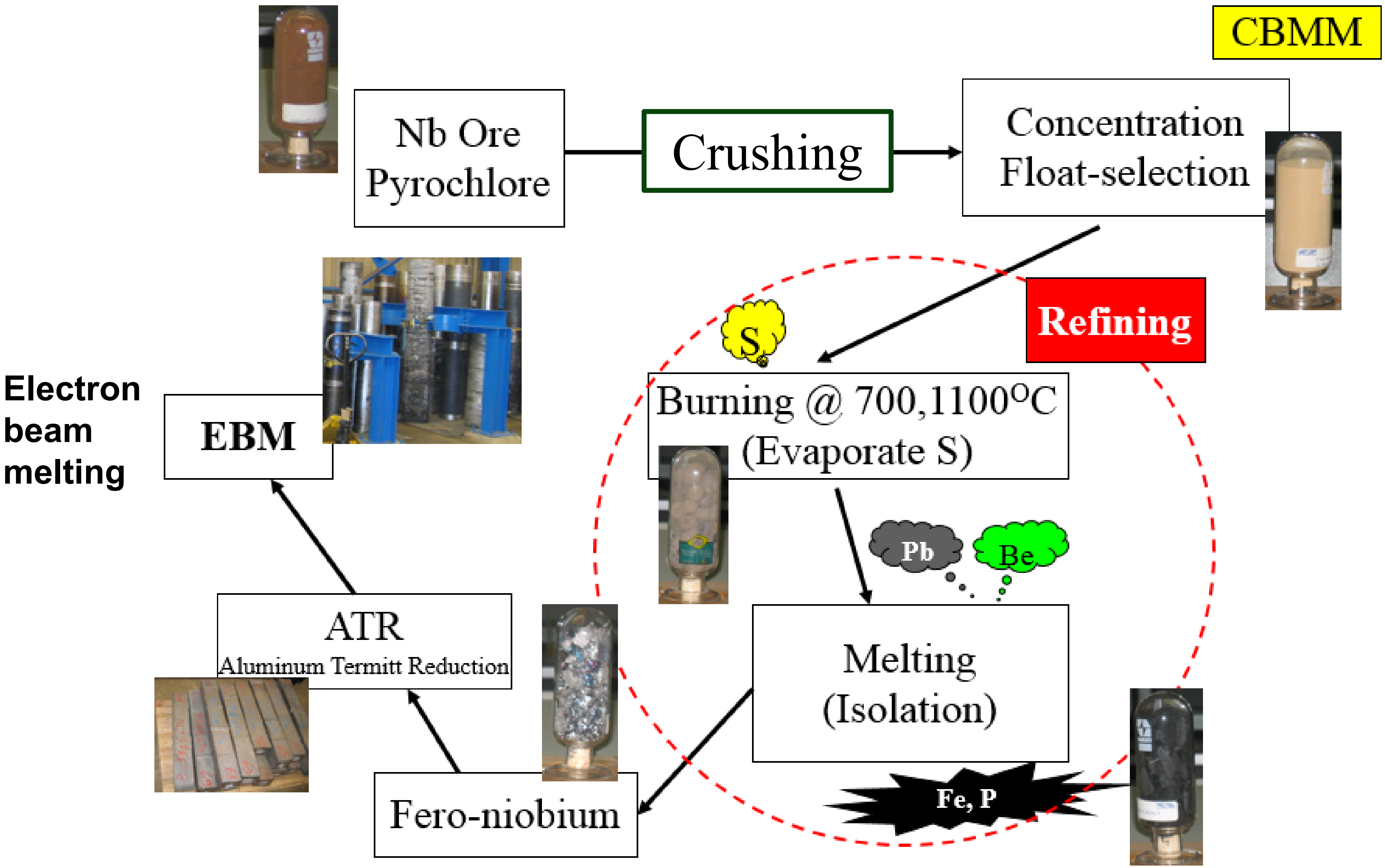
TEMIT reduction using electric furnace

↓

Ferro Nb

Niobium material production facility in CBMM (Brazil)

Niobium material production process in CBMM



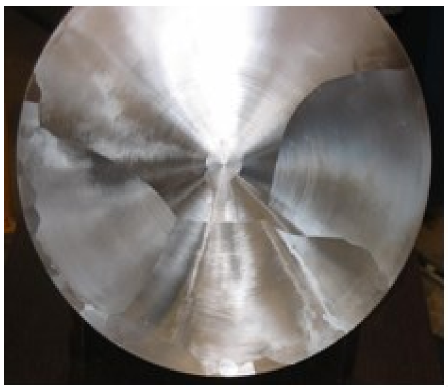
Refining process in CBMM

Nb Ore

After concentrated (55%)

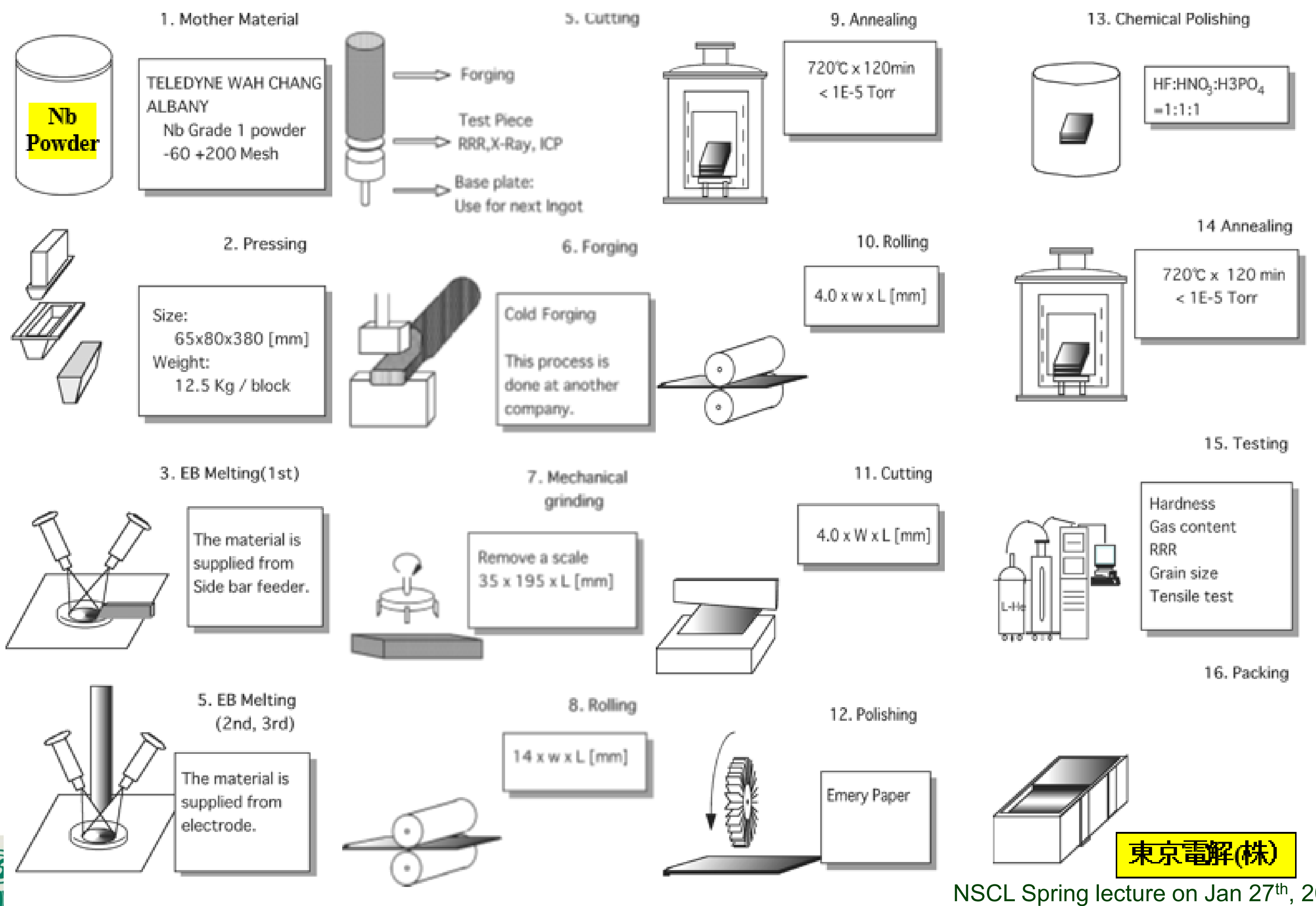
Pellets

Fero-niobium



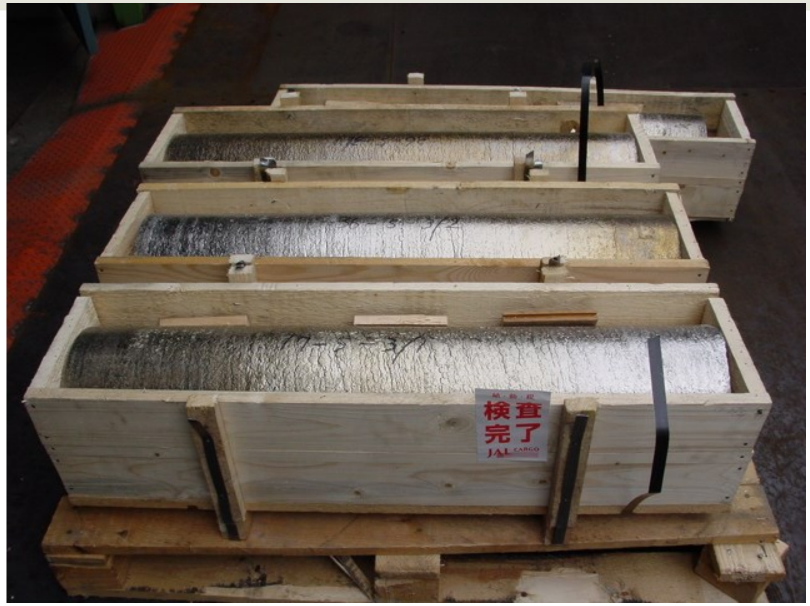
Large Grain Nb Ingot

6.3 Industrial high purity Nb sheet production (Tokyo Denkai company, Japan)



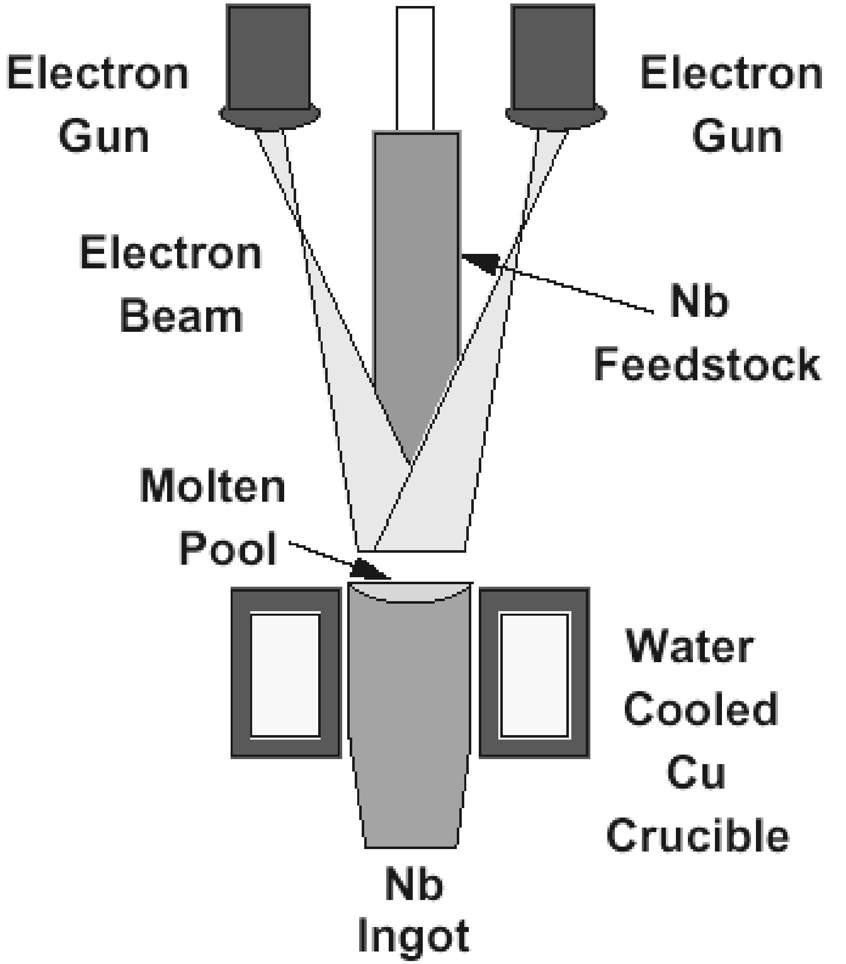
Primary Nb material for high purity Nb sheets

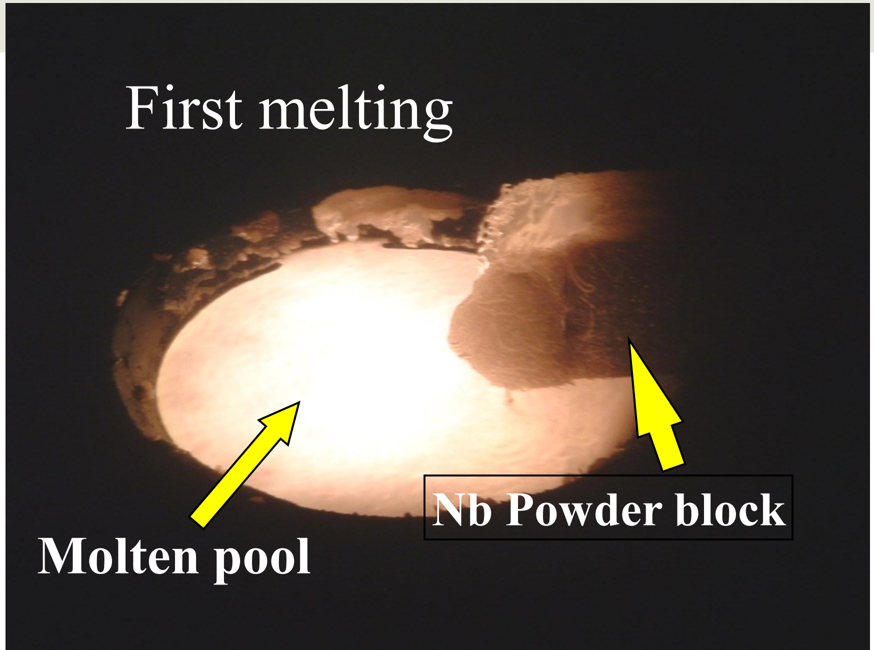
Tokyo Denkai

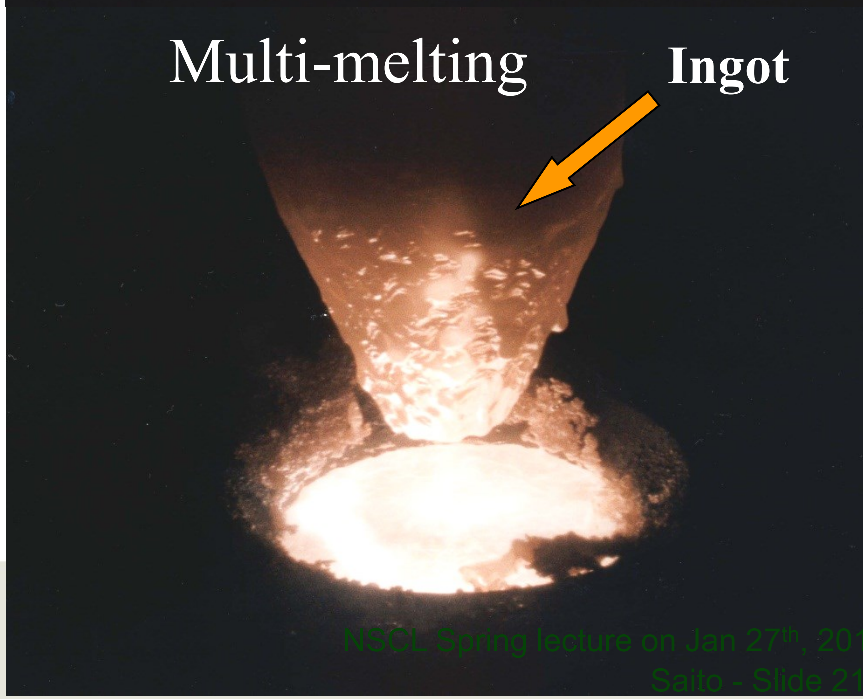


- The main metal impurity in niobium material is Tantalum because the chemical properties of these two metals are very similar.
- Special chemical isolation technique between Nb and Ta is required for high purity niobium material.
- This technology was disclosed from the nuclear weapon technology after Soviet Union destroyed.
- Now Silmet Co. in Estonia produces high purity primary Nb ingots.

Electron Beam Melting (EBM)

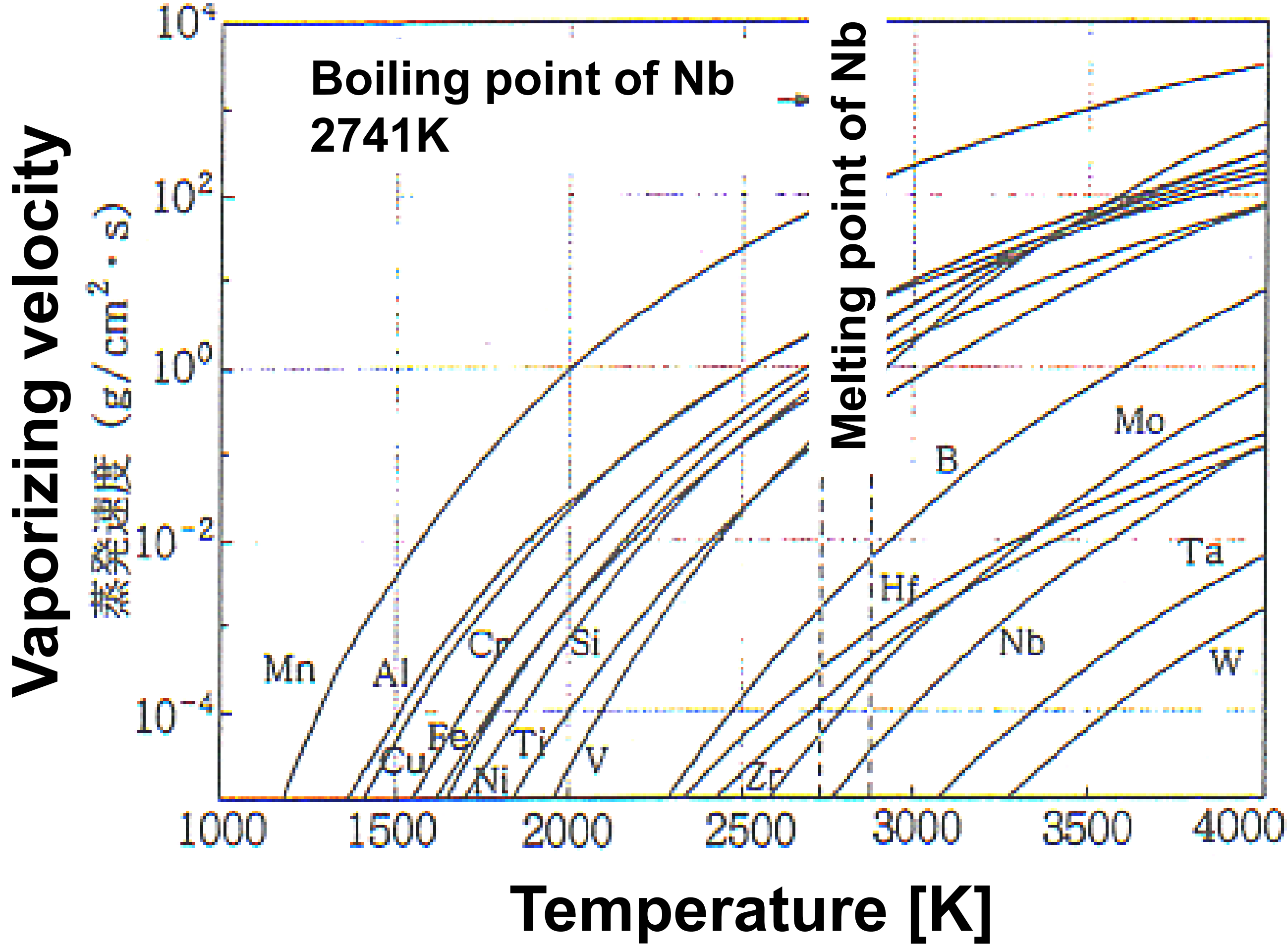






Niobium powder block

Why EBM is used for Nb purification



- Light metal are all evaporated below meting temperature of Nb
- Heavy metal elements: Mo, Ta, W remains as impurities.

Vapor pressure of impurities in the Nb material

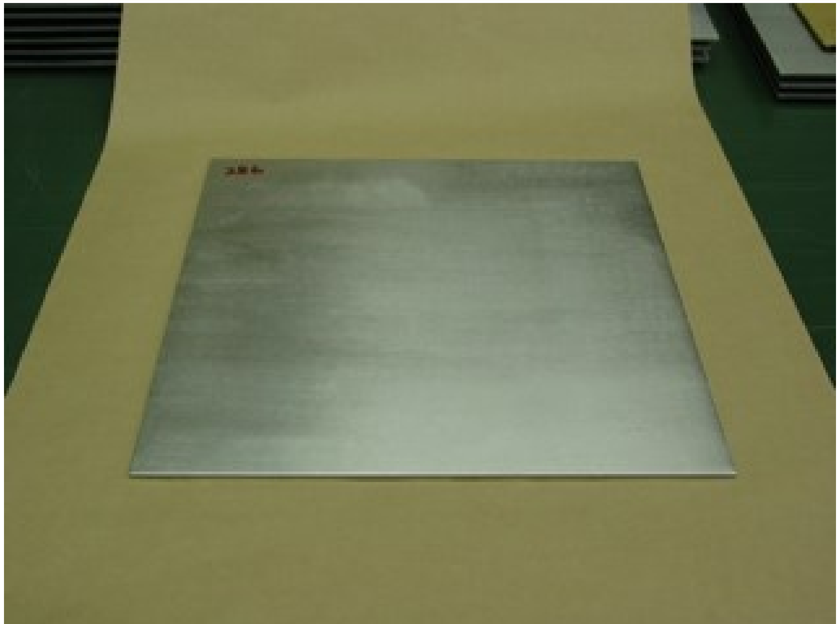
Electron beam melting (EBM) facility (Tokyo Denkai)

400kw EBM furnace

Nb Ingot post EBM

450 kg

Nb sheets (Tokyo Denkai)

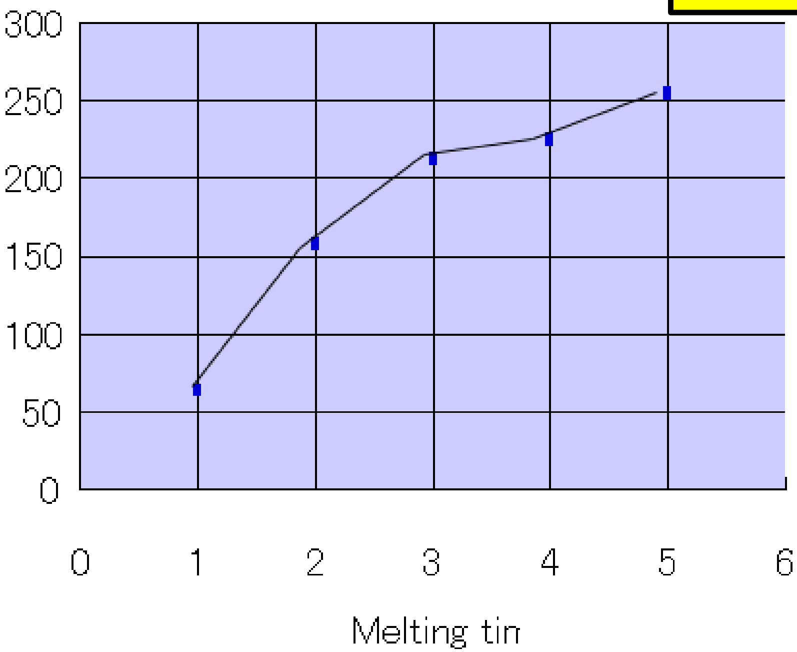


Nb sheets for KEK ILC R&D cavities

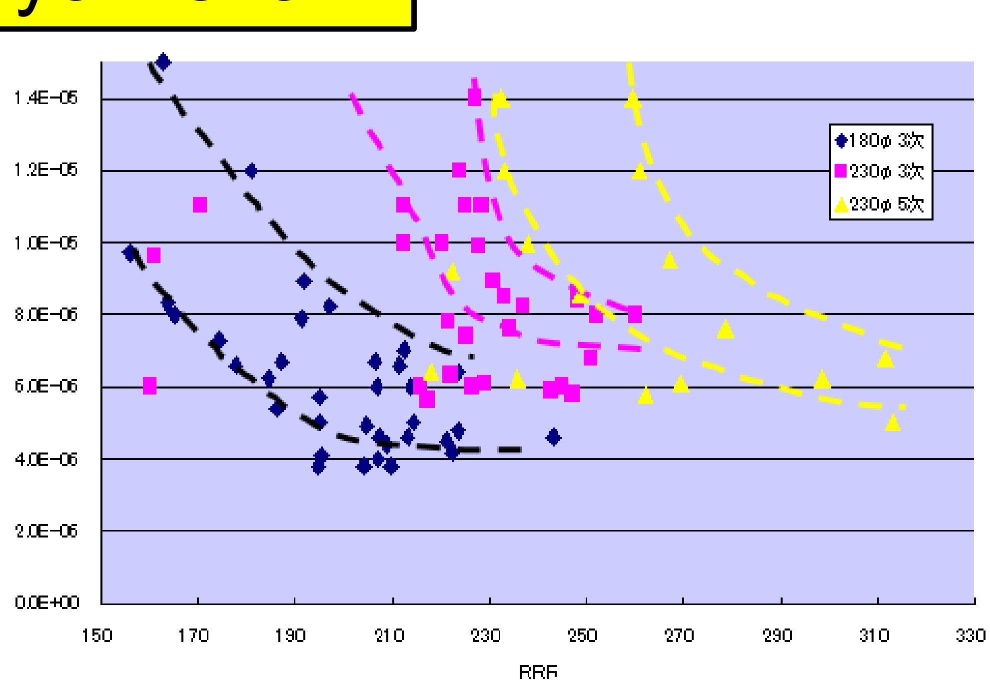
Key technique: high purity Nb ingot production

1) High quality vacuum pressure ⇨ Facility cost
2) Multiple electron beam melting
 ⇨ No required facility change
3) Large molten pool surface ⇨ Facility change, Large ingot

Tokyo Denaki



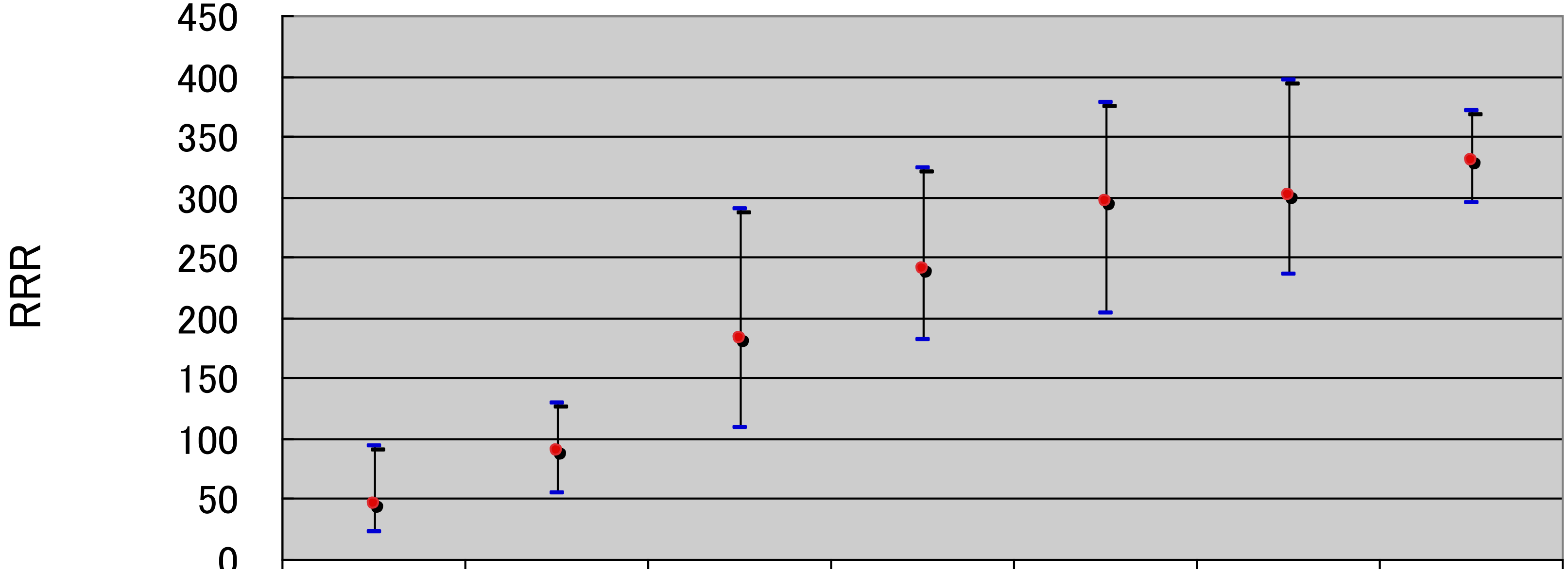
Effect of the multi-melting



Effect of the vacuum

Impact of multiple EB Melting

Change of RRR over melting times

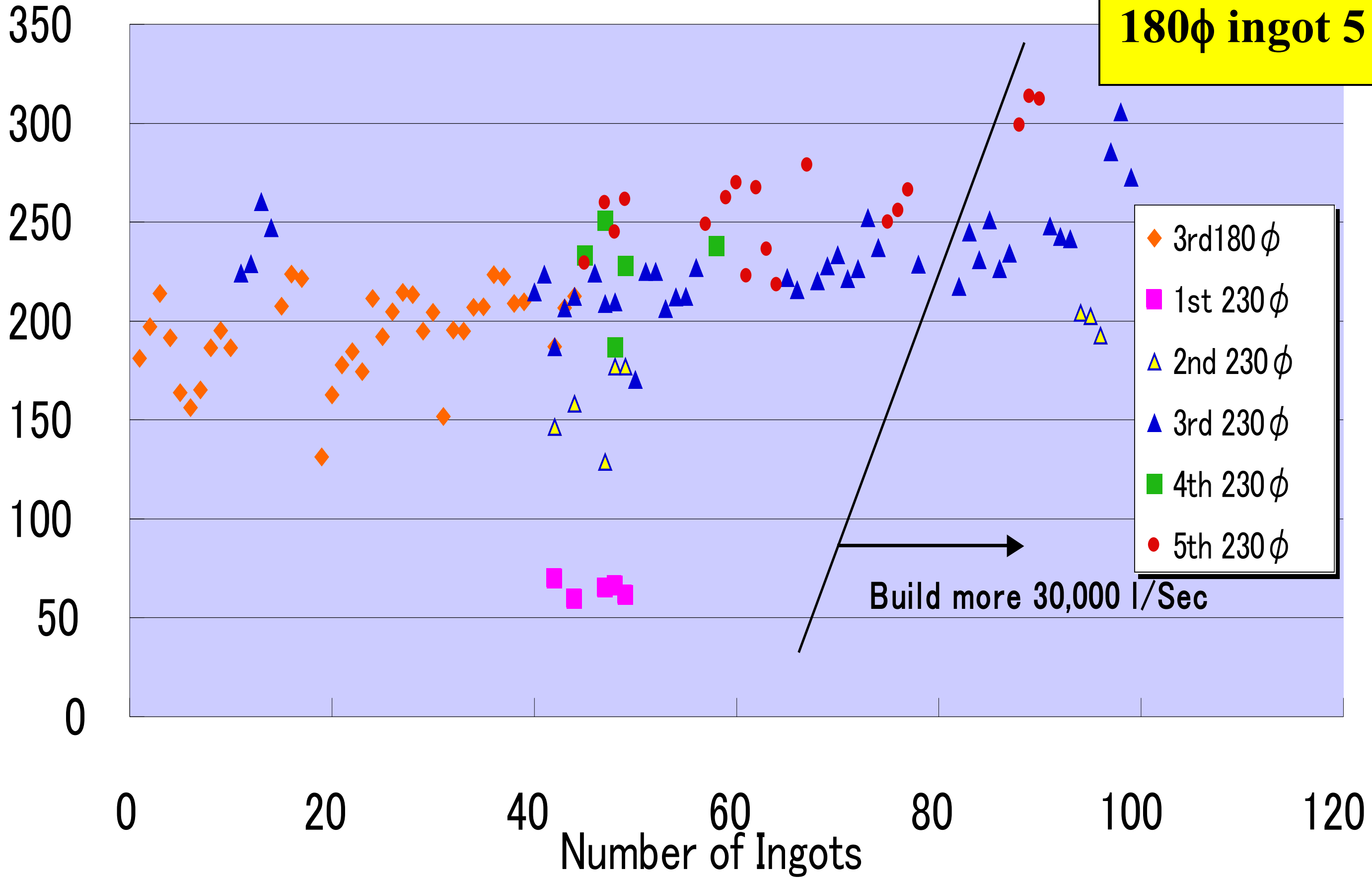


	A/R	1	2	3	4	5	6
Max	93	128	289	323	378	396	370
Average	46	90	183	240	296	301	329
Min	23	54	109	181	202	235	295

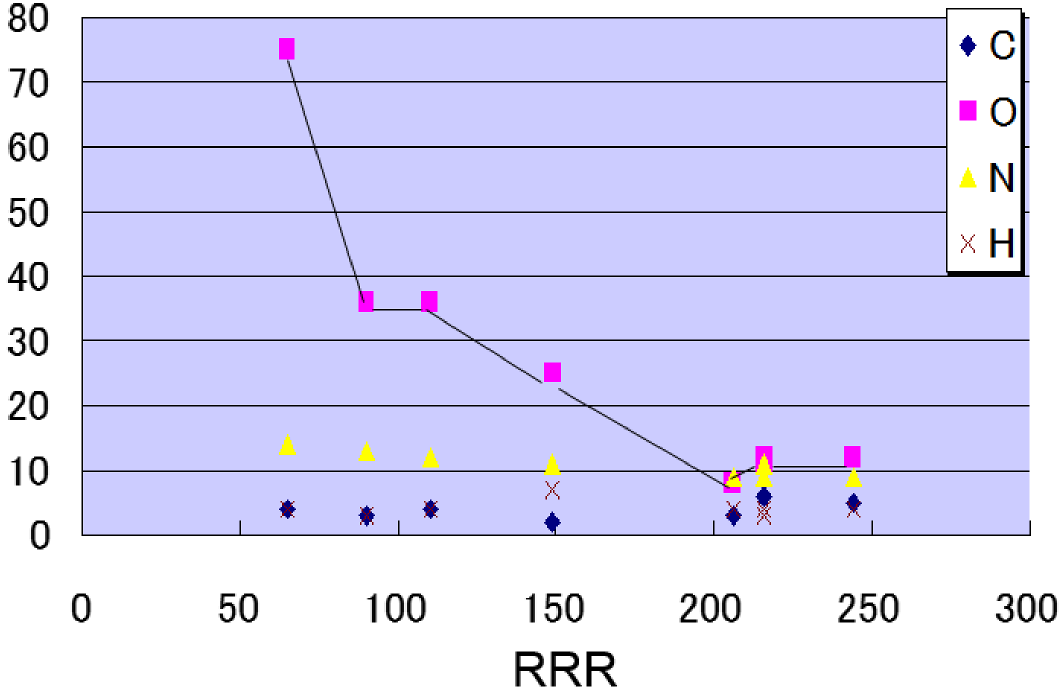
Melting Cycles

Impact of ingot diameter

Tokyo Denkai
Post adding 30000l/sec vac. pump
230ϕ ingot 3 times melting
180ϕ ingot 5 times melting $\Big\}$ **RRR=300**



Impurities in the RRR grade Nb ingot



- Oxygen is the main impurity in Low RRR Nb material.
- RRR > 200, Oxygen and Nitrogen are main impurity, ~ 10 ppm
- RRR can be estimated by the impurity concentration

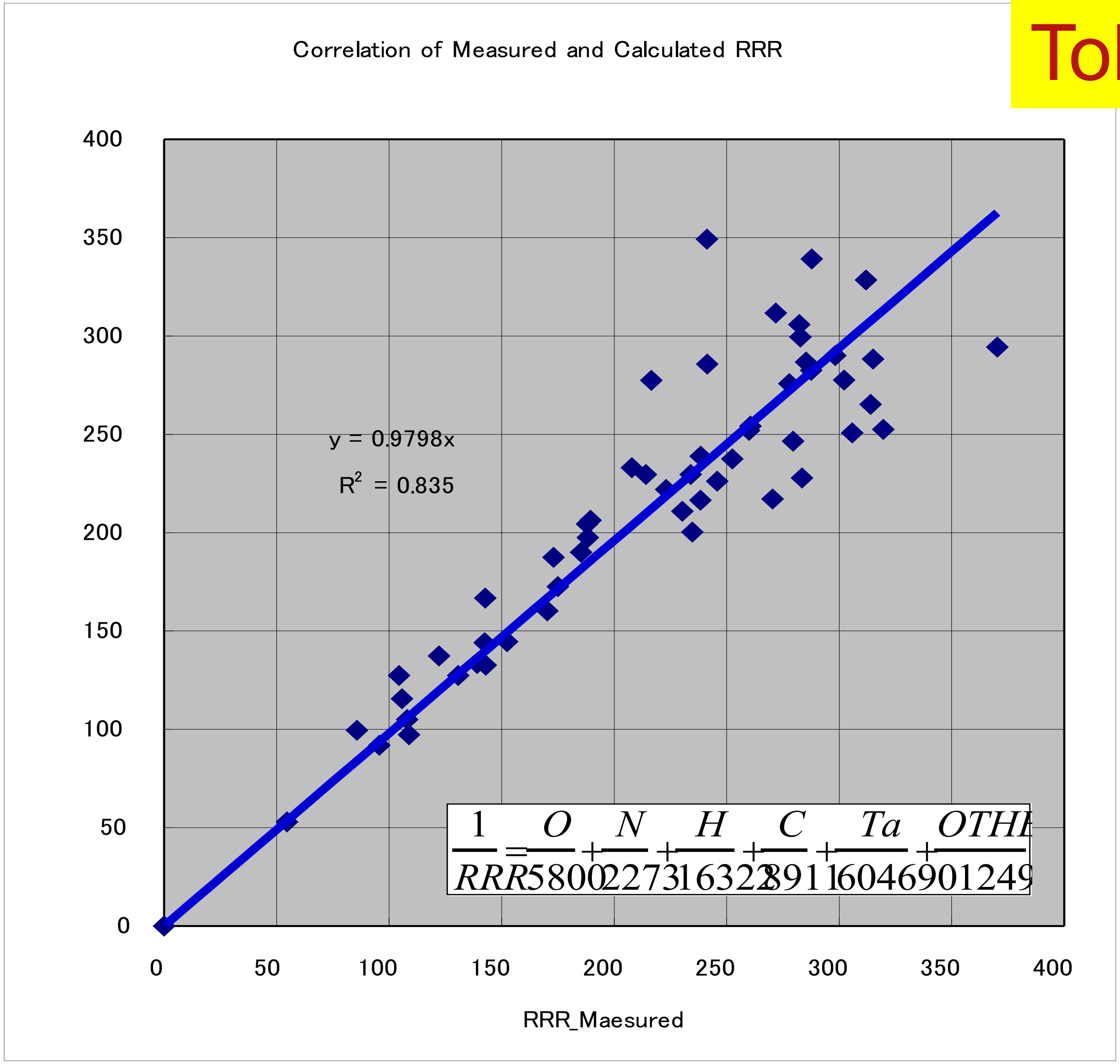
$$\frac{1}{RRR} = \frac{C_H}{1500} + \frac{C_C}{4100} + \frac{C_N}{3900} + \frac{C_O}{5000} + \cdots + \frac{C_{Ta}}{550000} + \cdots$$

Example: $C_H = 1ppm, C_C = 5ppm, C_N = 5ppm, C_O = 7ppm$, $Ta = 400ppm$ (purity: 99.9582%)

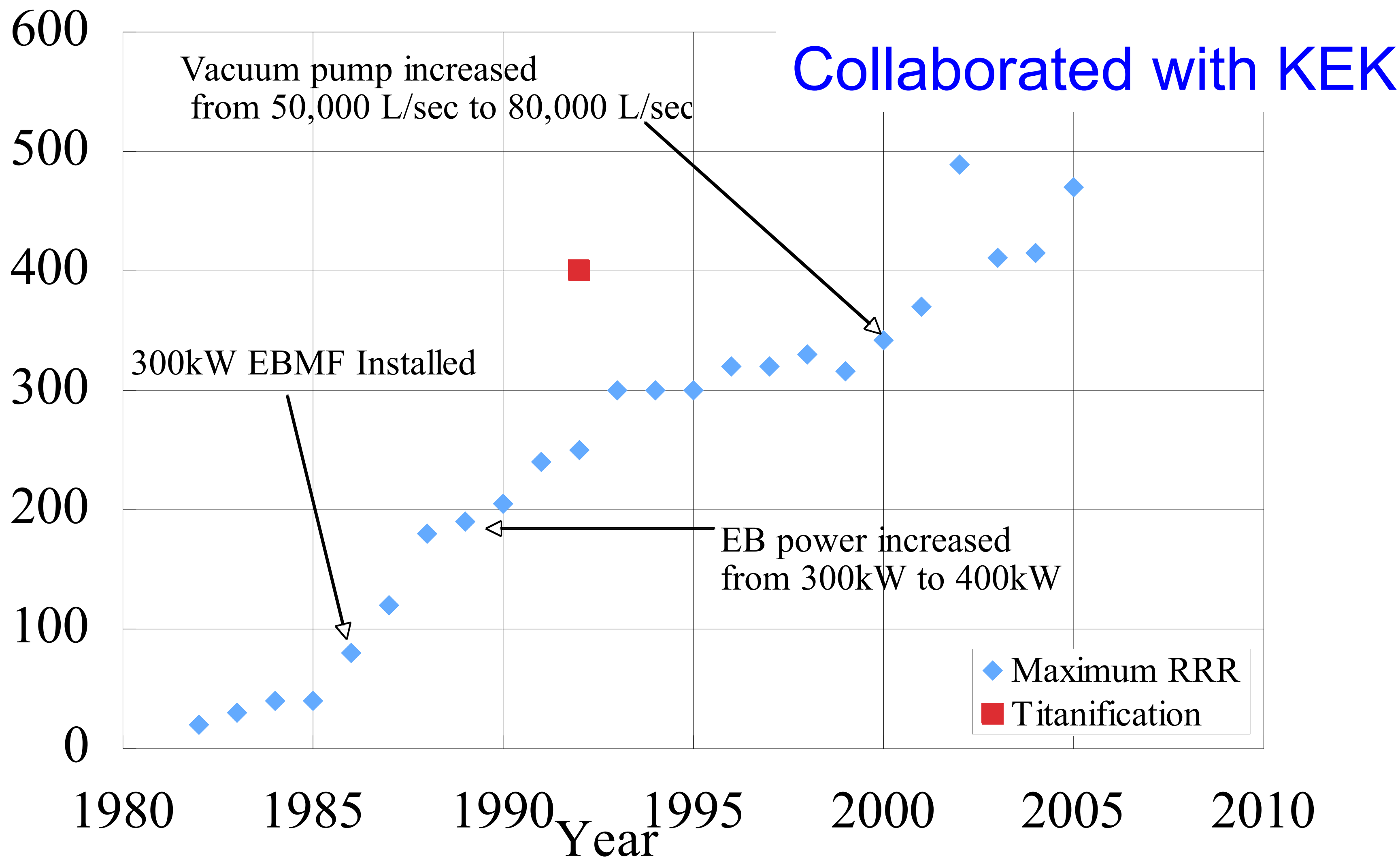
$$\frac{1}{RRR} = \frac{1}{1500} + \frac{5}{4100} + \frac{5}{3900} + \frac{7}{5000} + \frac{400}{550000}, \qquad RRR = 188.8$$

Relationship between RRR and Impurity concentration

Tokyo Denkai



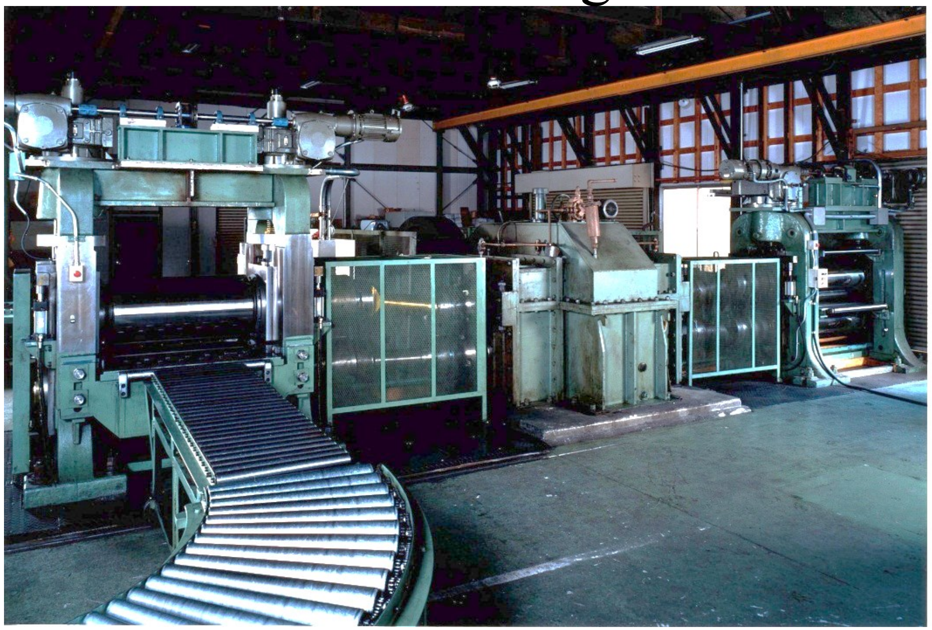
Improvement of RRR in the Industrial Nb Ingot (Tokyo Denkai)



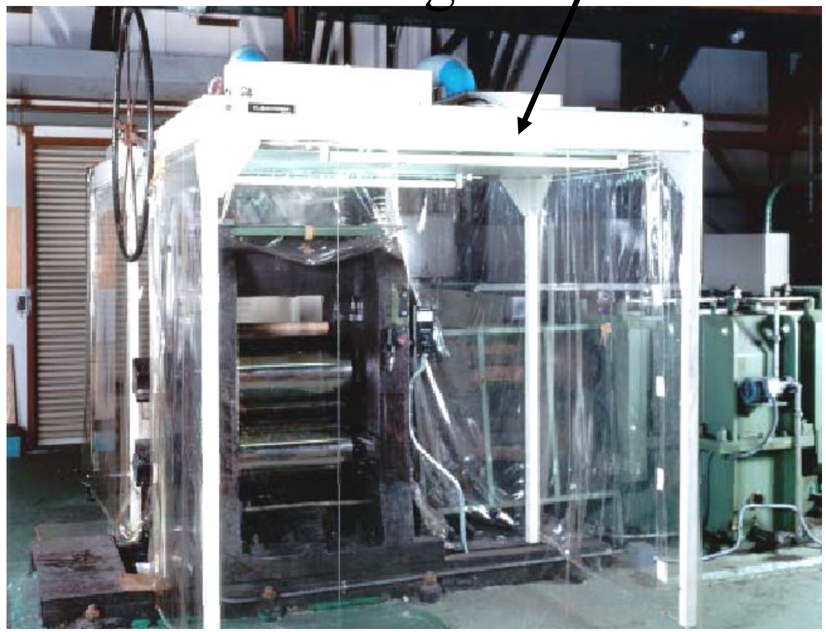
Nb sheet production facility (Tokyo Denkai)

Cleanroom

Intermediate rolling



Final rolling



Effort to dust not biting in the Nb sheets

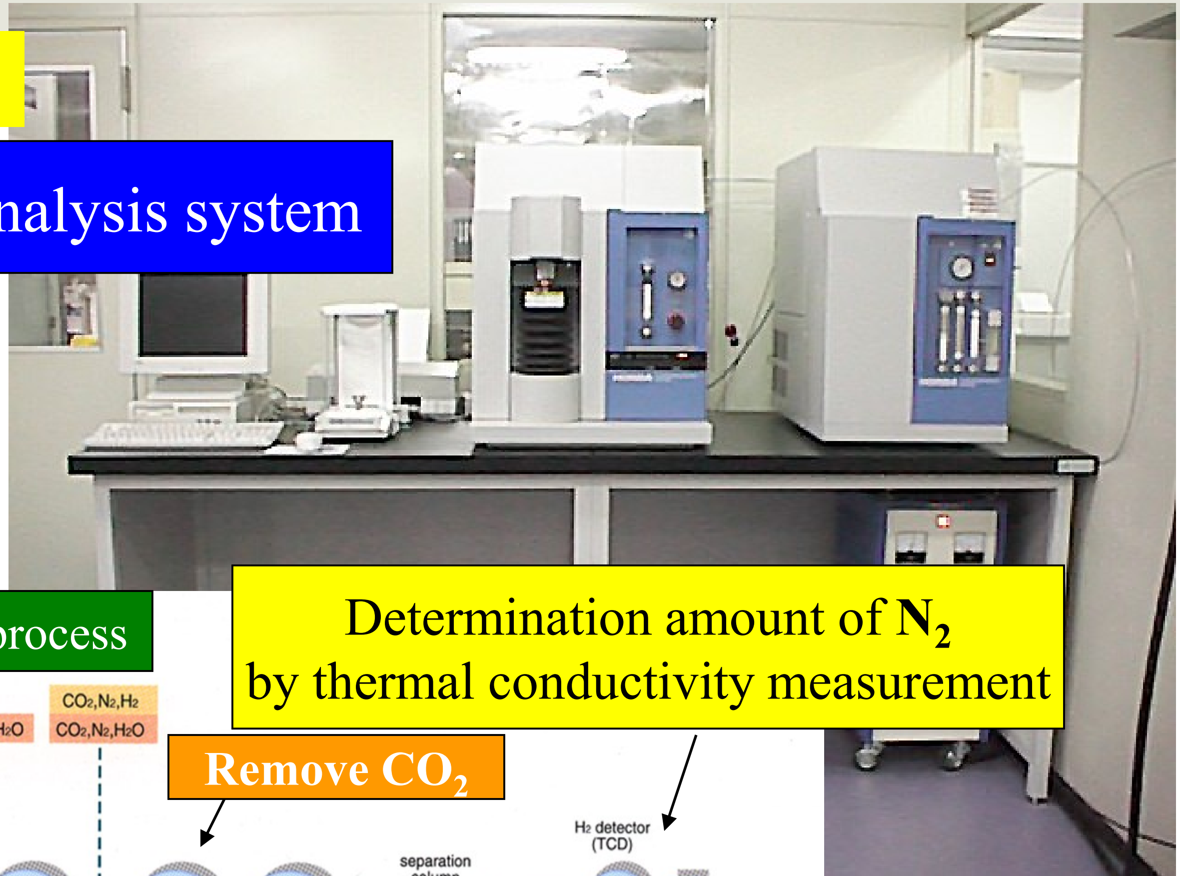
Vacuum annealing furnace

Tokyo Denkai
1400^{o}C Max,
~1x10^{-6} Torr
Effective working zone
1000ϕ x 1800L
Ta heater

6.4 Quality Control (Gas Analysis; H, N, O)

Tokyo Denkai

Oxygen・Nitrogen gas analysis system



Case of N_2

Sample Flow

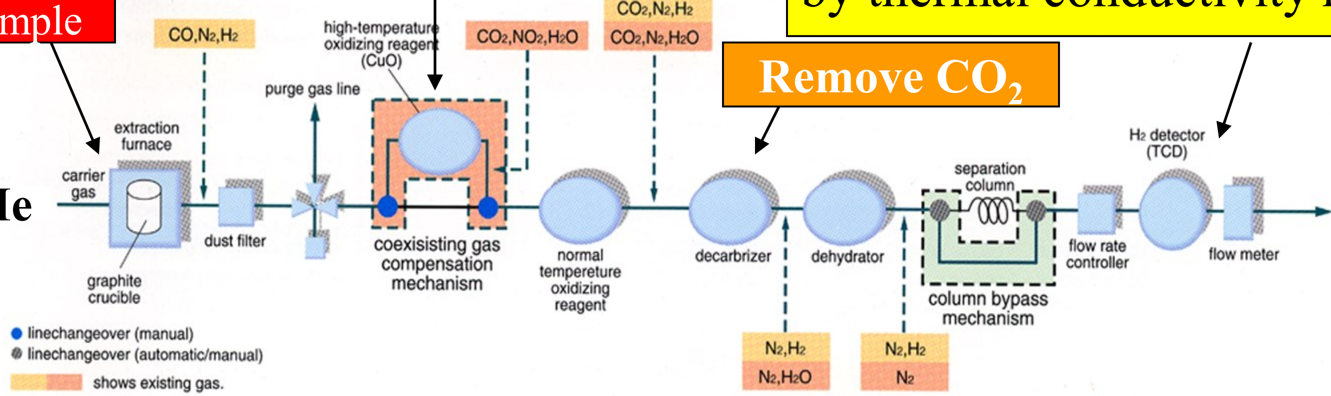
Oxidization process

Determination amount of N_2 by thermal conductivity measurement

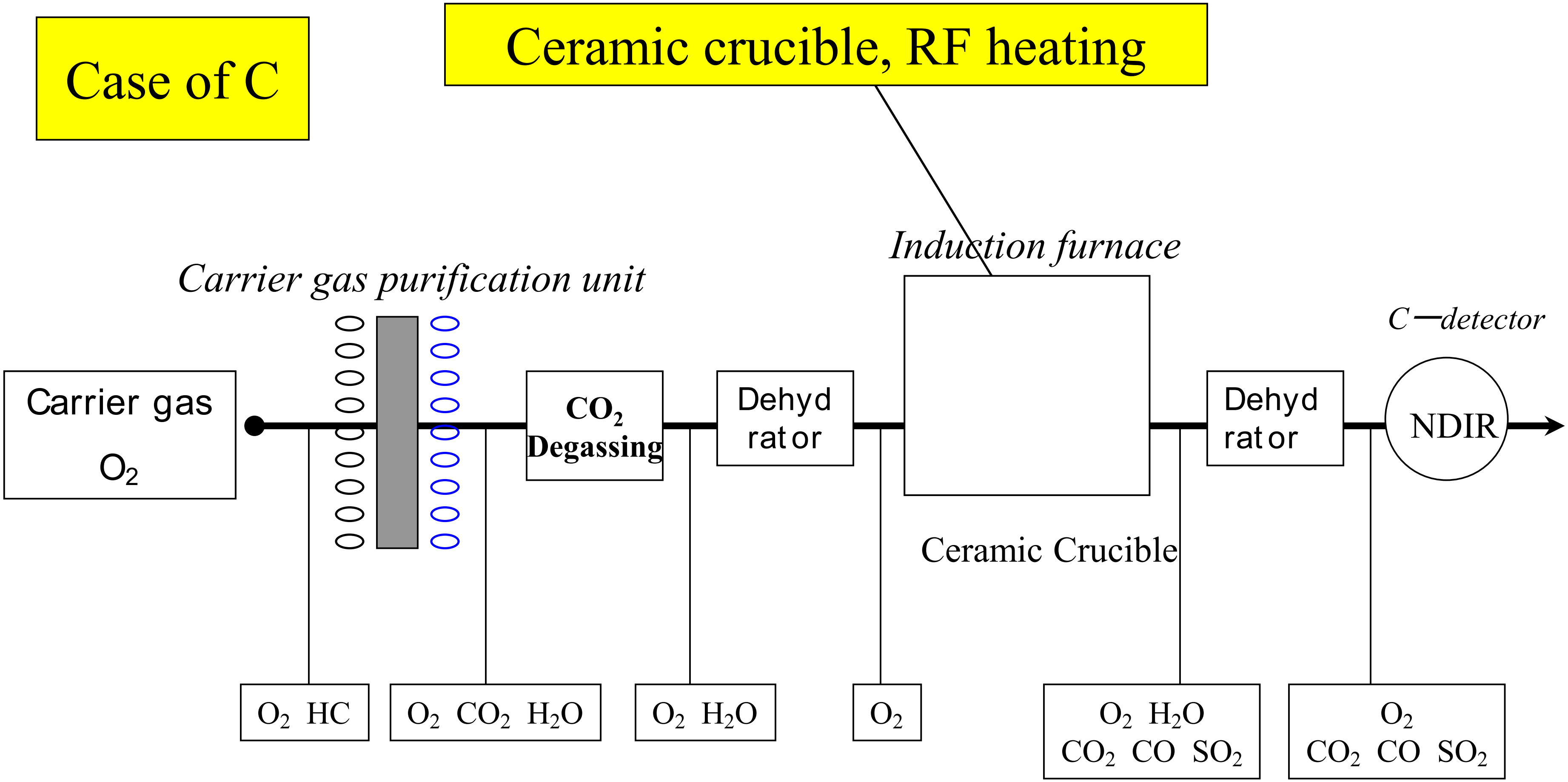
Sample

Remove CO_2

He

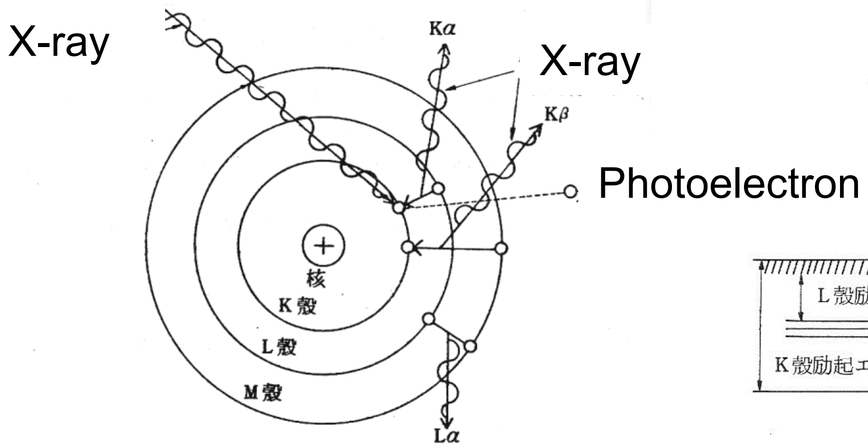


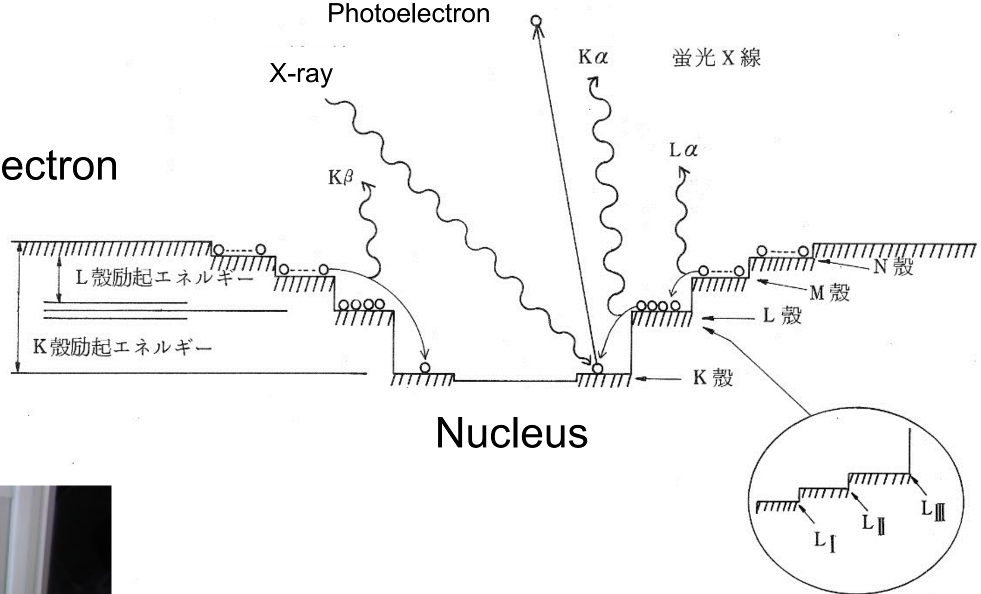
Analysis of Carbon contamination



Other contamination analysis

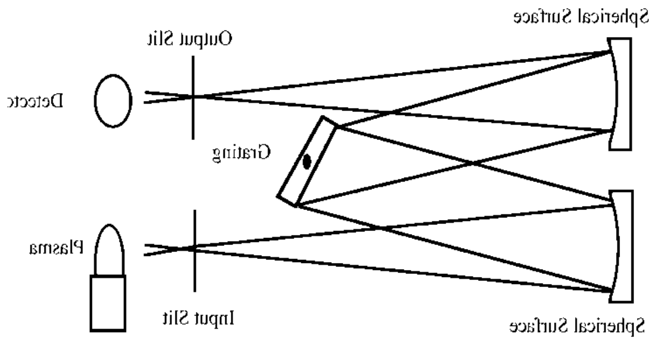
X-ray Fluorescence Analysis system

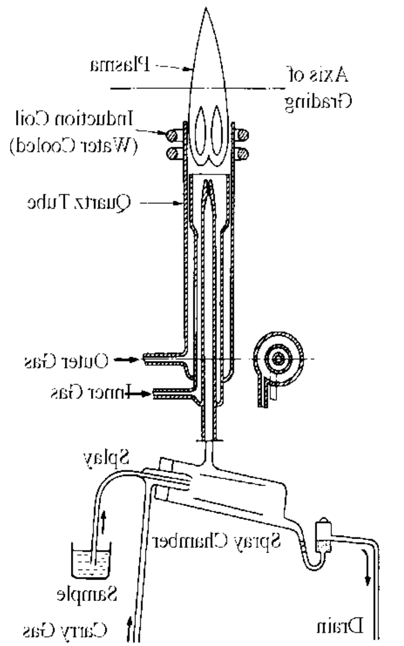




Tokyo Denkai

ICP-OES Analysis

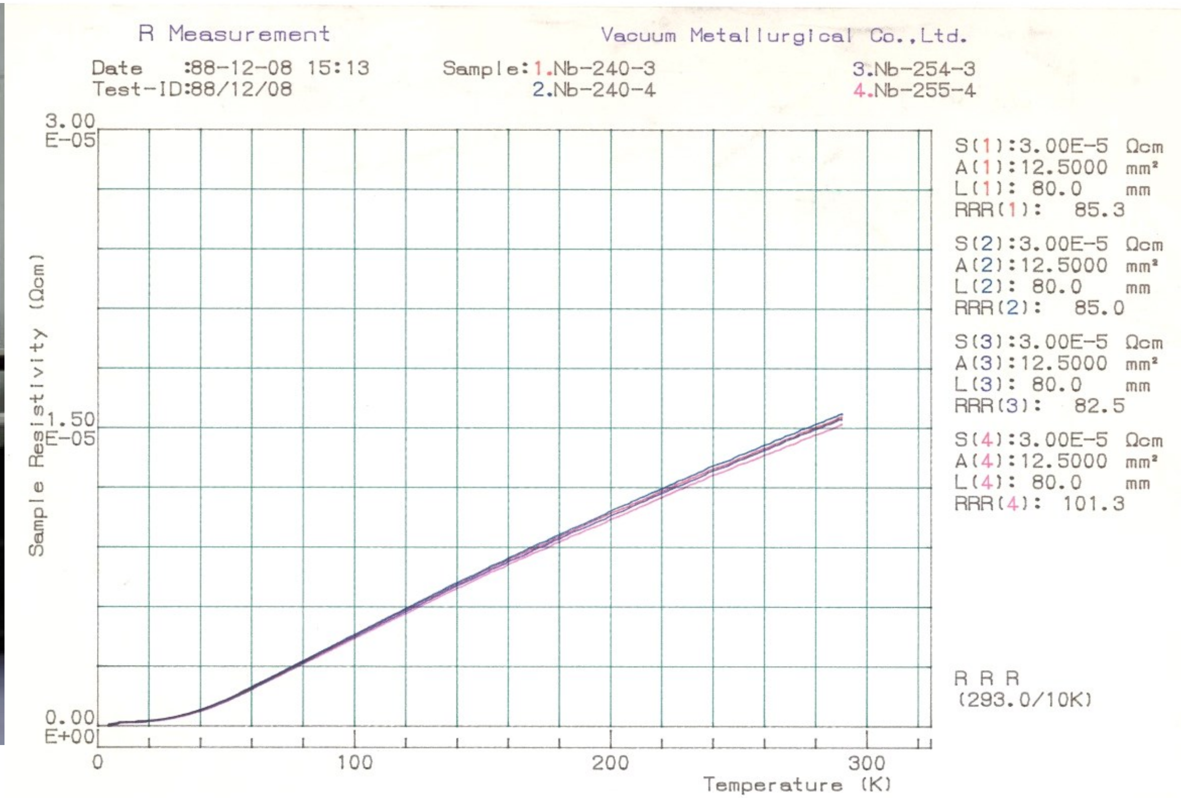




Tokyo Denkai

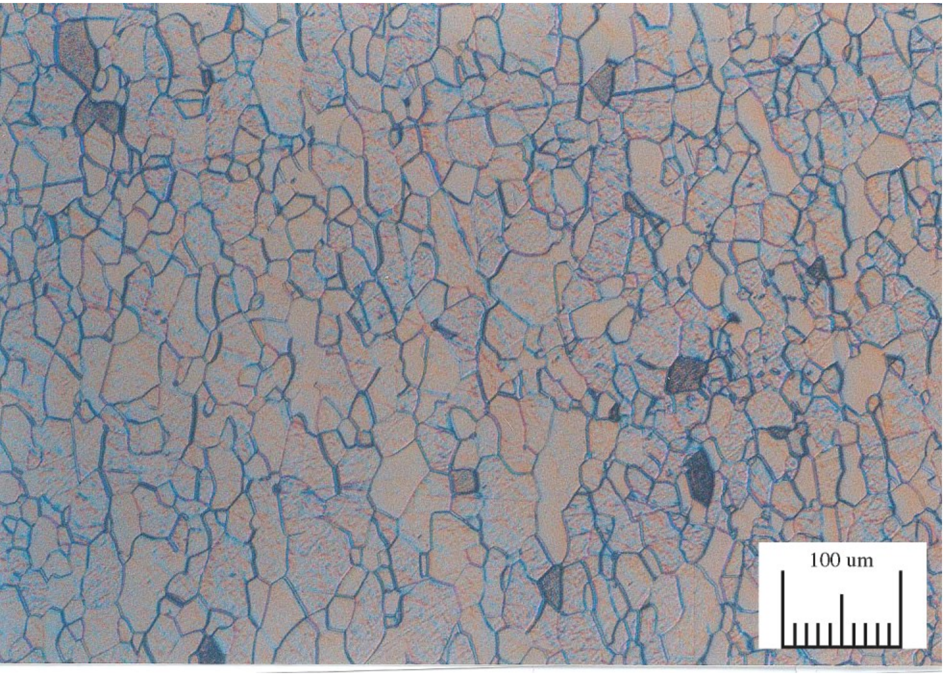
RRR measurement

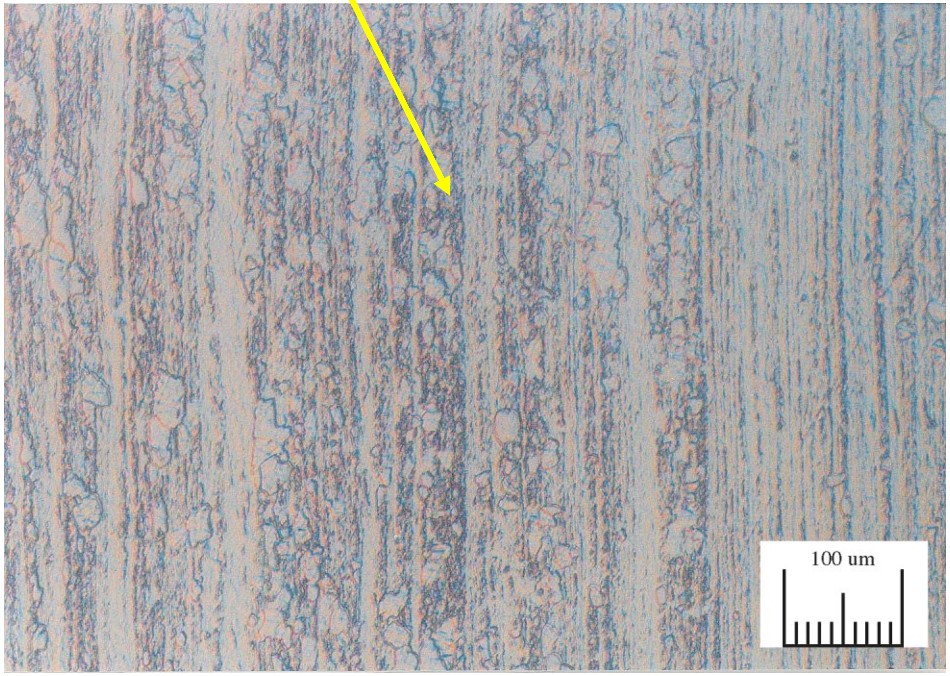
Tokyo Denkai



Grain control

Rolled structure can be seen



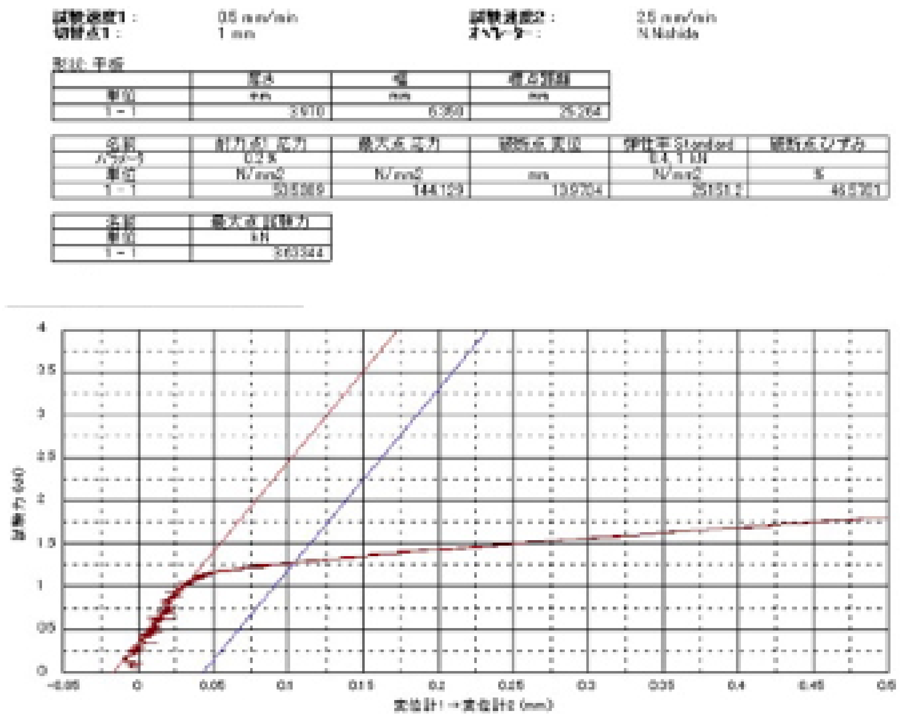


Well annealed Nb sample

None annealed Nb sample

Tensile Test Machine

東京電解（株）



Tensile Test

Nb 引張試験結果
未完全な再結晶

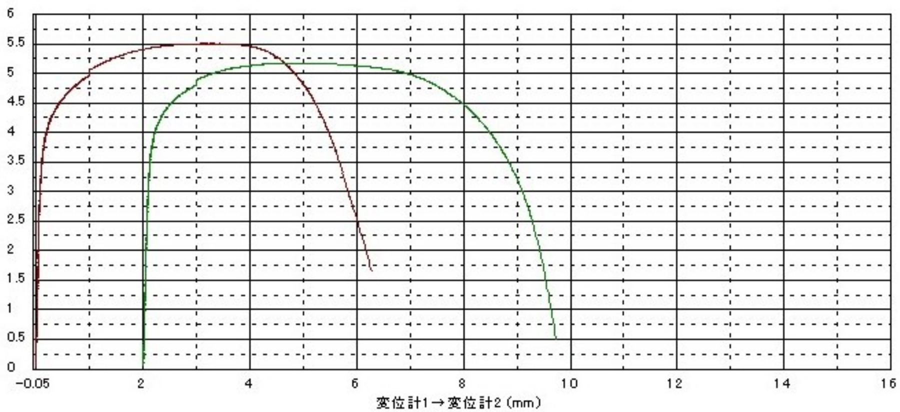
験速度1： 0.5 mm/min　　試験速度2： 2.5 mm/min
替点1： 1 mm　　オペレーター： N.Nishida

状: 平板

	厚さ	幅	標点距離
単位	mm	mm	mm
1 - 1	3.940	6.340	25.276
1 - 2	3.990	6.340	25.408

名前	耐力点1_応力	最大点_応力	破断点_変位	弾性率_Standard	破断点_ひずみ
パラメータ	0.2 %			1, 3 kN	
単位	N/mm2	N/mm2	mm	N/mm2	%
1 - 1	152.924	220.692	6.28125	41259.5	20.9375
1 - 2	150.786	204.733	7.73281	37860.0	25.7760

名前	最大点_試験力
単位	kN
1 - 1	5.51281
1 - 2	5.17906



Not well annealed Nb sample

Nb 引張試験結果
完全再結晶

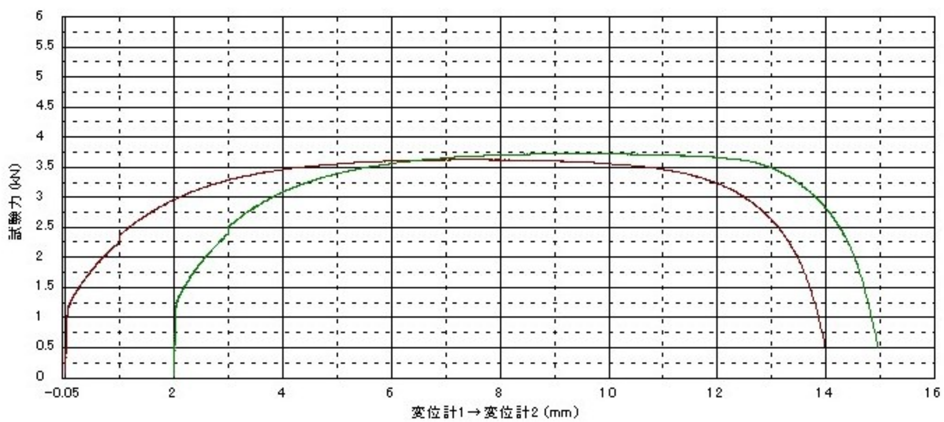
試験速度1： 0.5 mm/min　　試験速度2： 2.5 mm/min
切替点1： 1 mm　　オペレーター： N.Nishida

形状: 平板

	厚さ	幅	標点距離
単位	mm	mm	mm
1 - 1	3.970	6.350	25.264
1 - 2	3.970	6.340	25.480

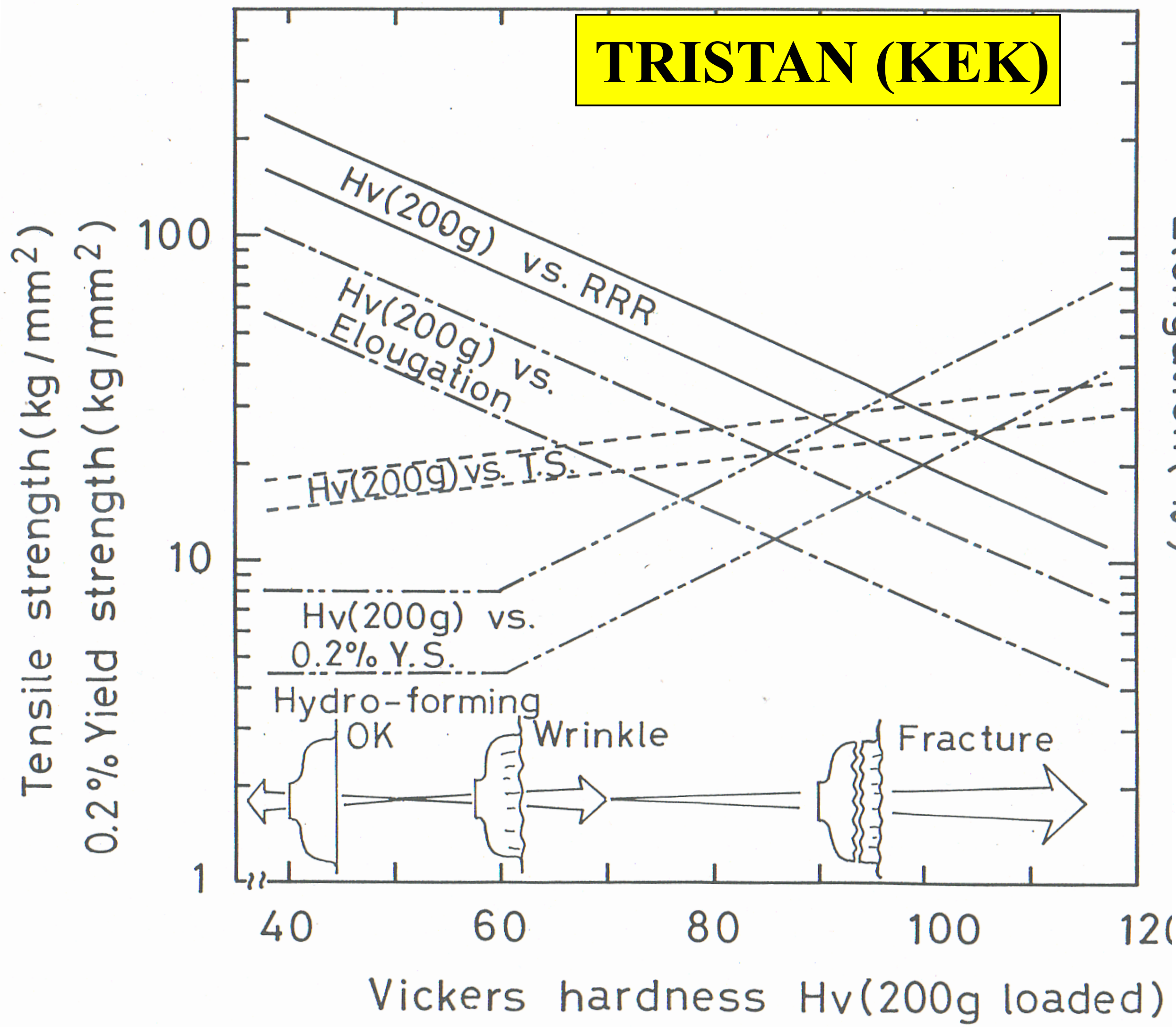
名前	耐力点1_応力	最大点_応力	破断点_変位	弾性率_Standard	破断点_ひずみ
パラメータ	0.2 %			0.4, 1 kN	
単位	N/mm2	N/mm2	mm	N/mm2	%
1 - 1	50.5389	144.129	13.9734	25151.2	46.5781
1 - 2	54.3061	148.280	12.9515	27900.9	43.1718

名前	最大点_試験力
単位	kN
1 - 1	3.63344
1 - 2	3.73219



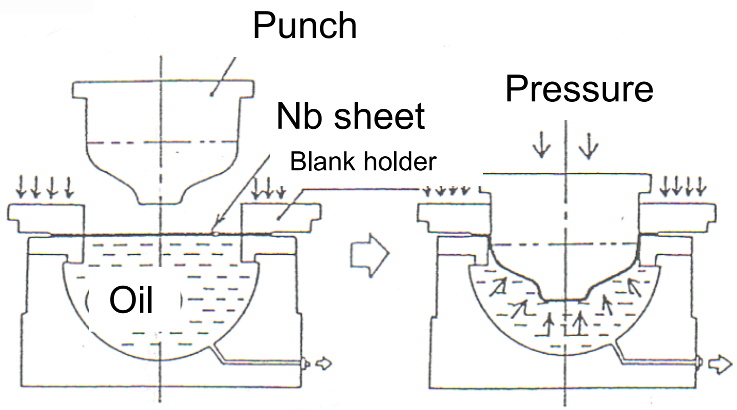
Well annealed Nb sample

Hardness vs mechanical properties



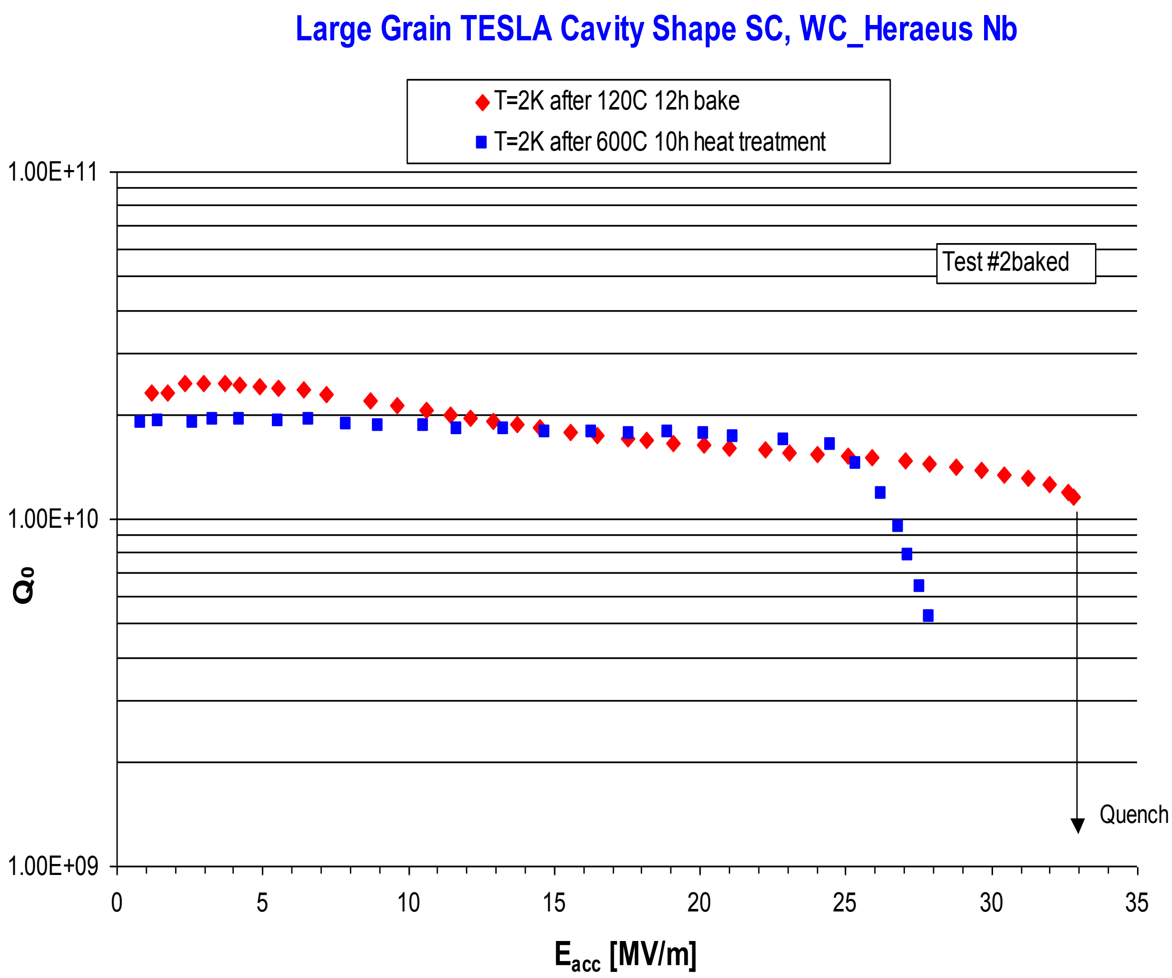
For successful hydroforming
H_V < 45。
RRR > 120
Elongation > 45%

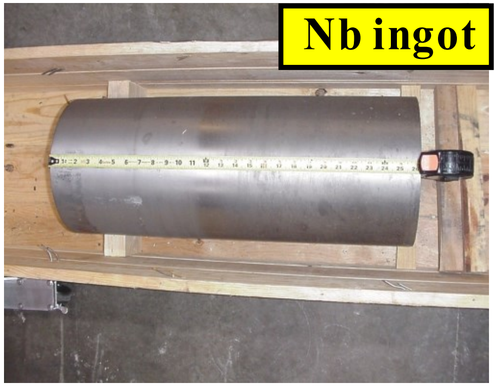
Hydroforming of TRISTAN cavity half cell

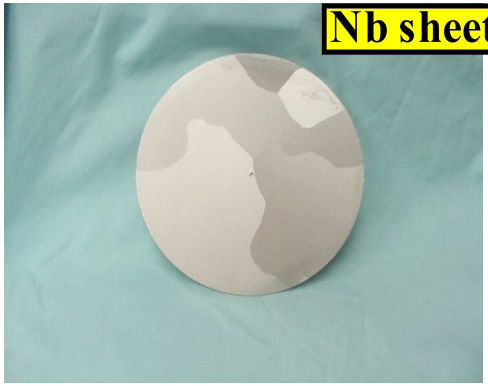


6.5 Advance sheet production for large grain cavities

Large grain niobium cavity R&D in Jlab







Large grain Nb sheet production can bring a cost down.
BCP could produce 35MV/m gradient and it brings further cost down.

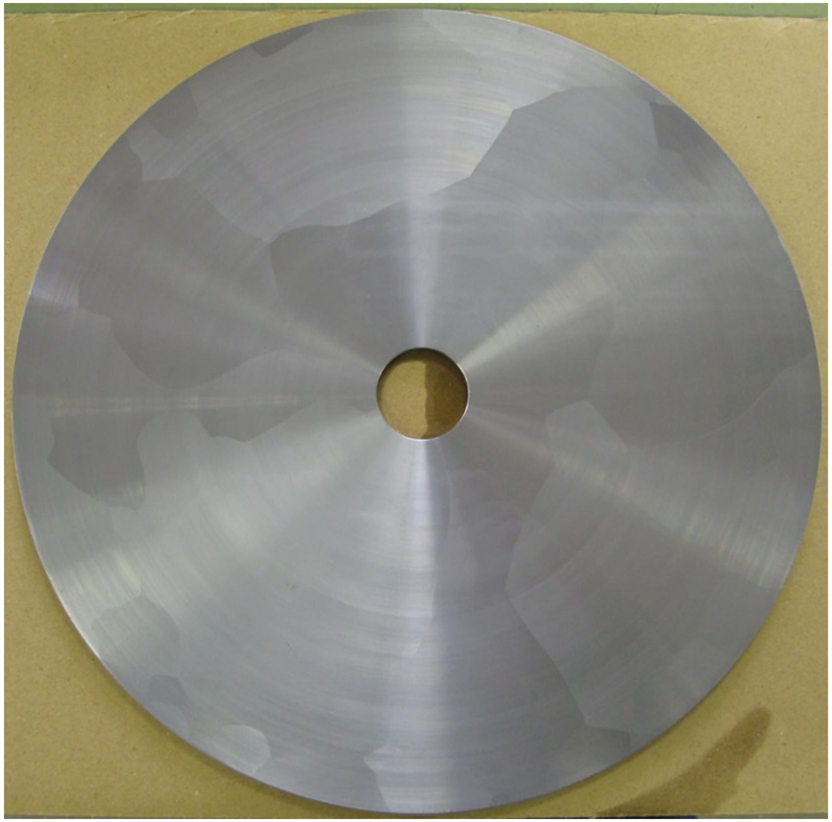
Early LG Nb sheet production

Sawing, thickness of saw ~2mm

- Loose lot of material
- Cutting surface is very rough and needs mechanical polishing

By H.Umezawa @東京電解

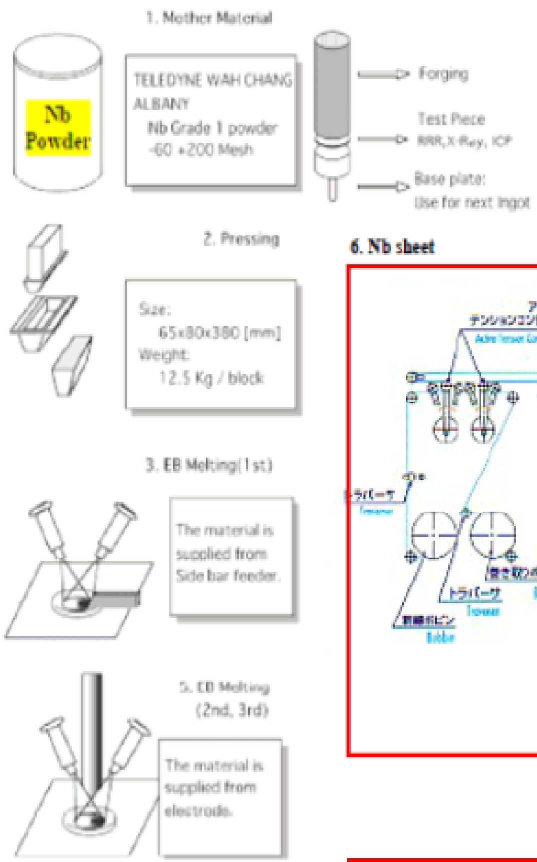
Post mechanical polishing



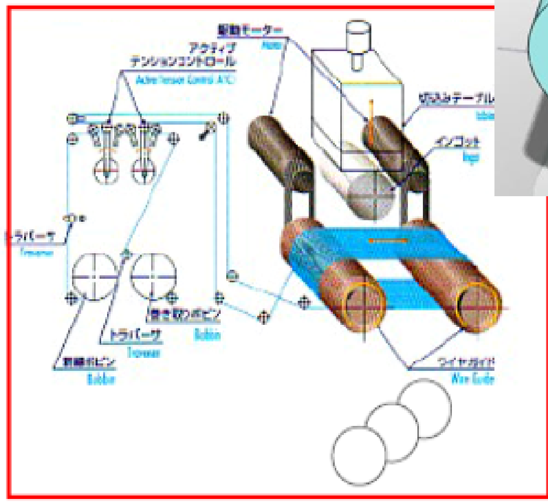
Multi-Wire Slicing Method

K.Saito

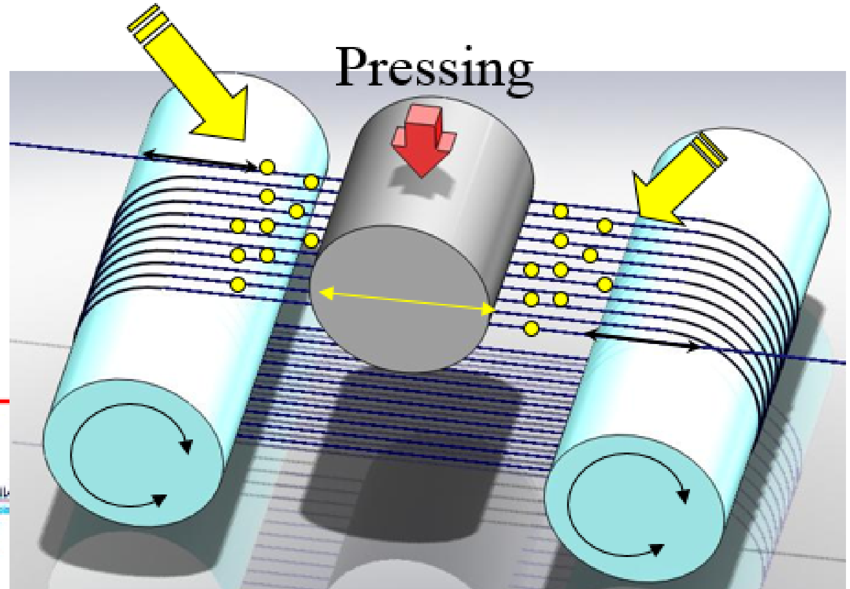
Single Crystal-Large Grain Niobium Technology Workshop in Brazil 2006



6. Nb sheet



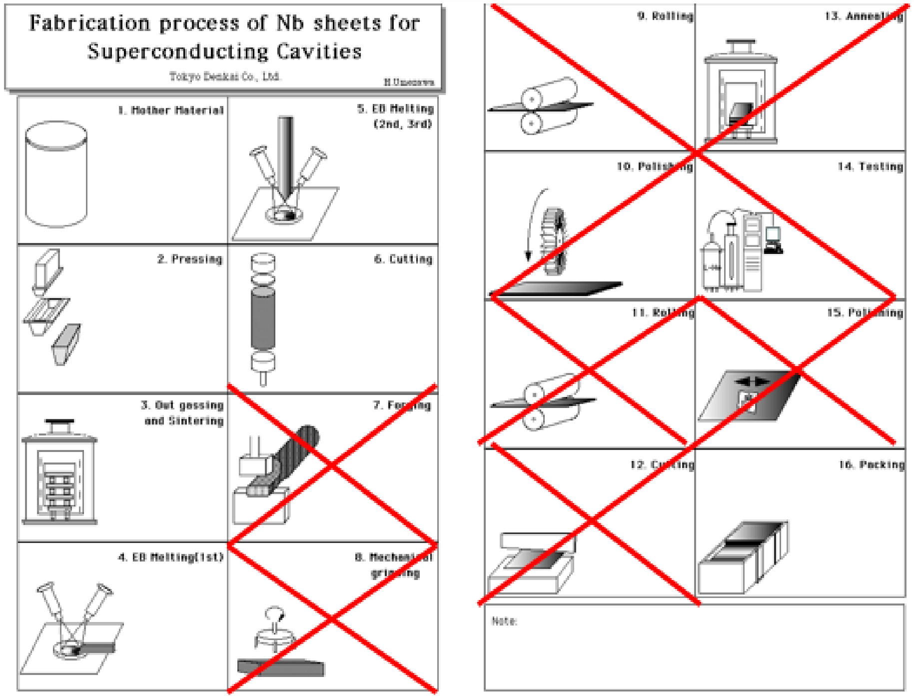
Splay liquid abrasives



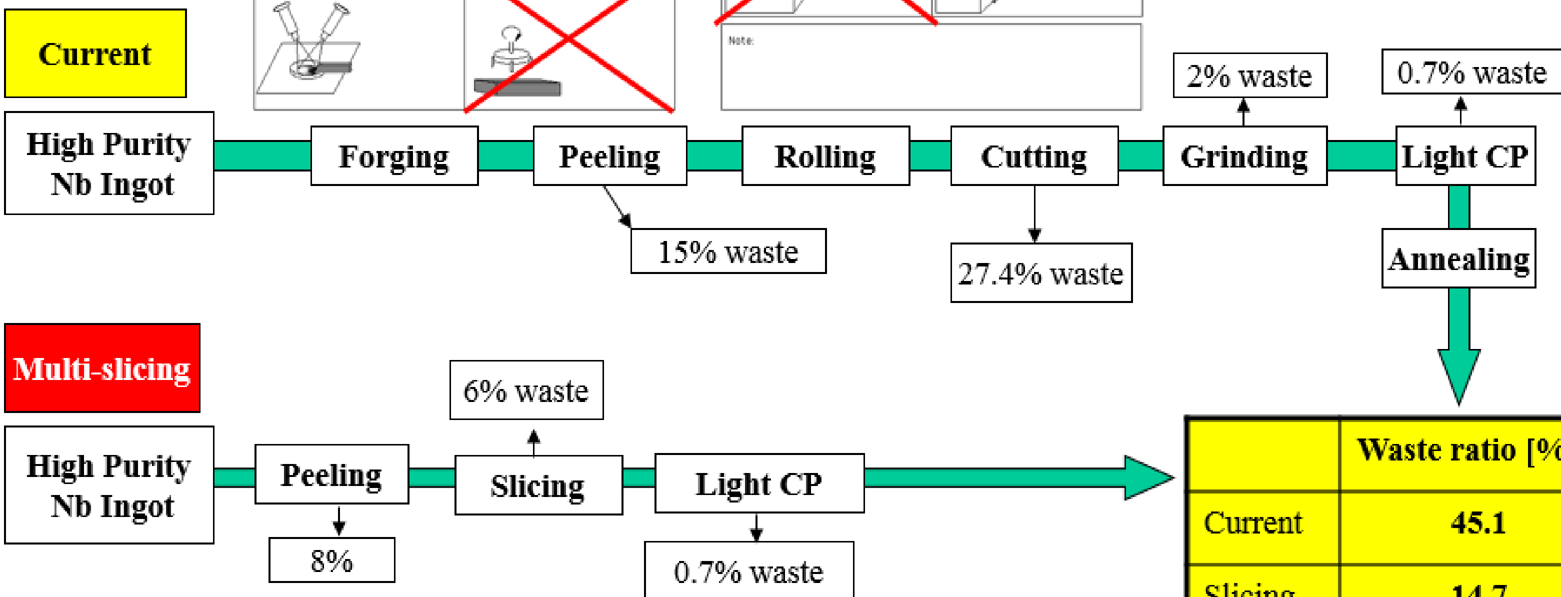
Slicing used very thin piano wire (0.16Φ) and liquid abrasive

This technology is well established on silicon wafer slicing.
However, the experts had very critical opinions about my idea.

Benefit of MW Slicing



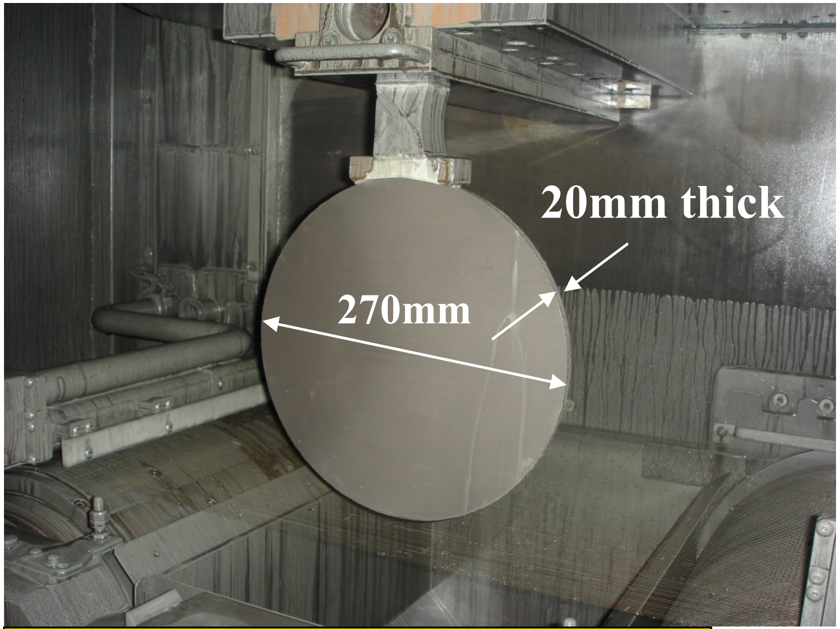
150sheets/3days, if 450L ingot is ready.



	Waste ratio [%]
Current	45.1
Slicing	14.7

Successfully Developed Wire Sawing Method for Nb Ingot

KEK/Tokyodenkai/Izumi-tech

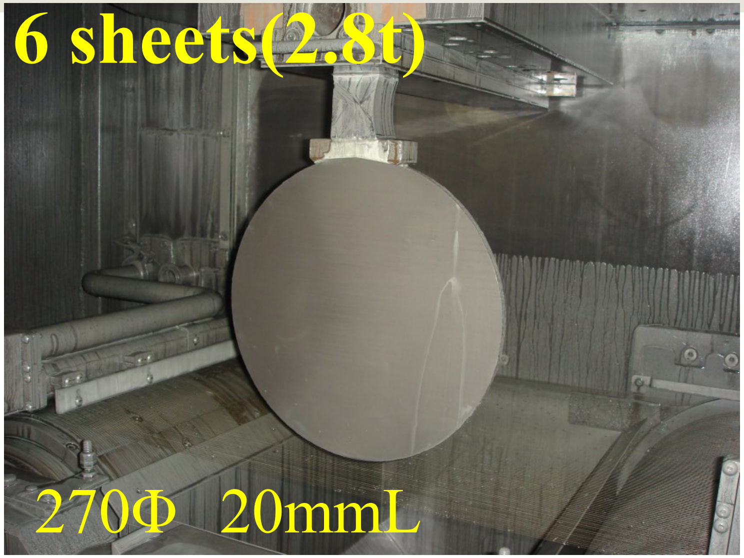


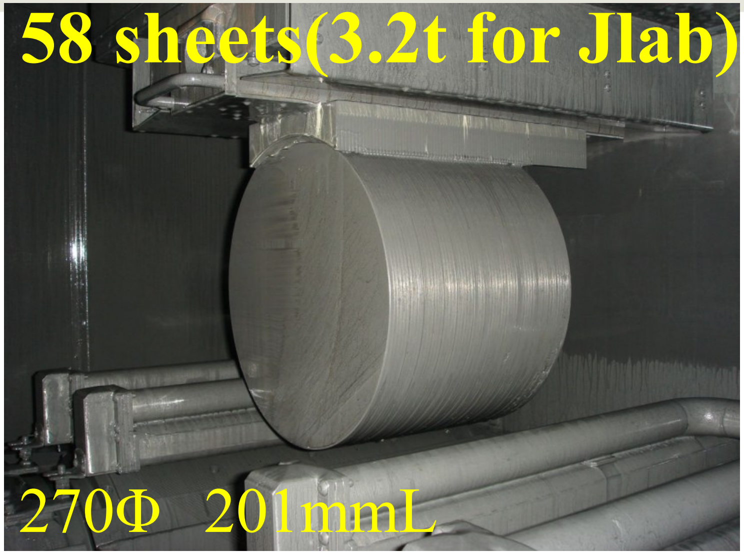
Processing time : 39 hr

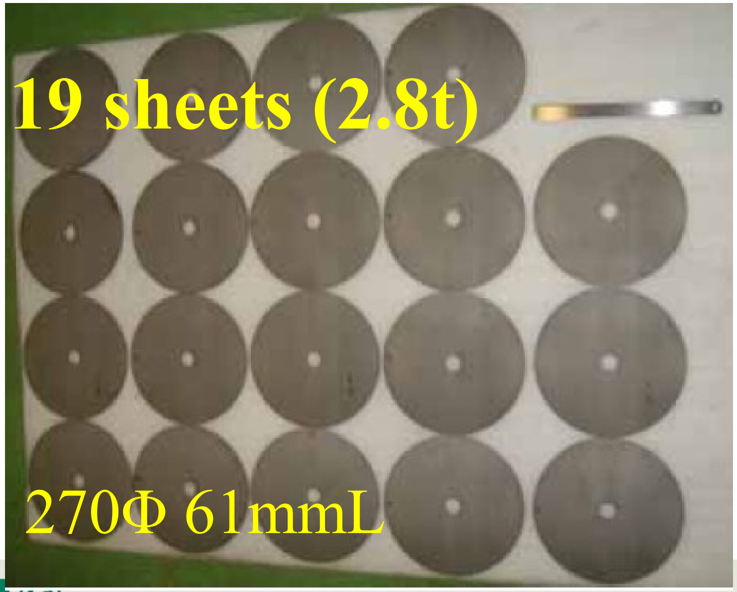
39

LG Nb ingot wire sawing sample

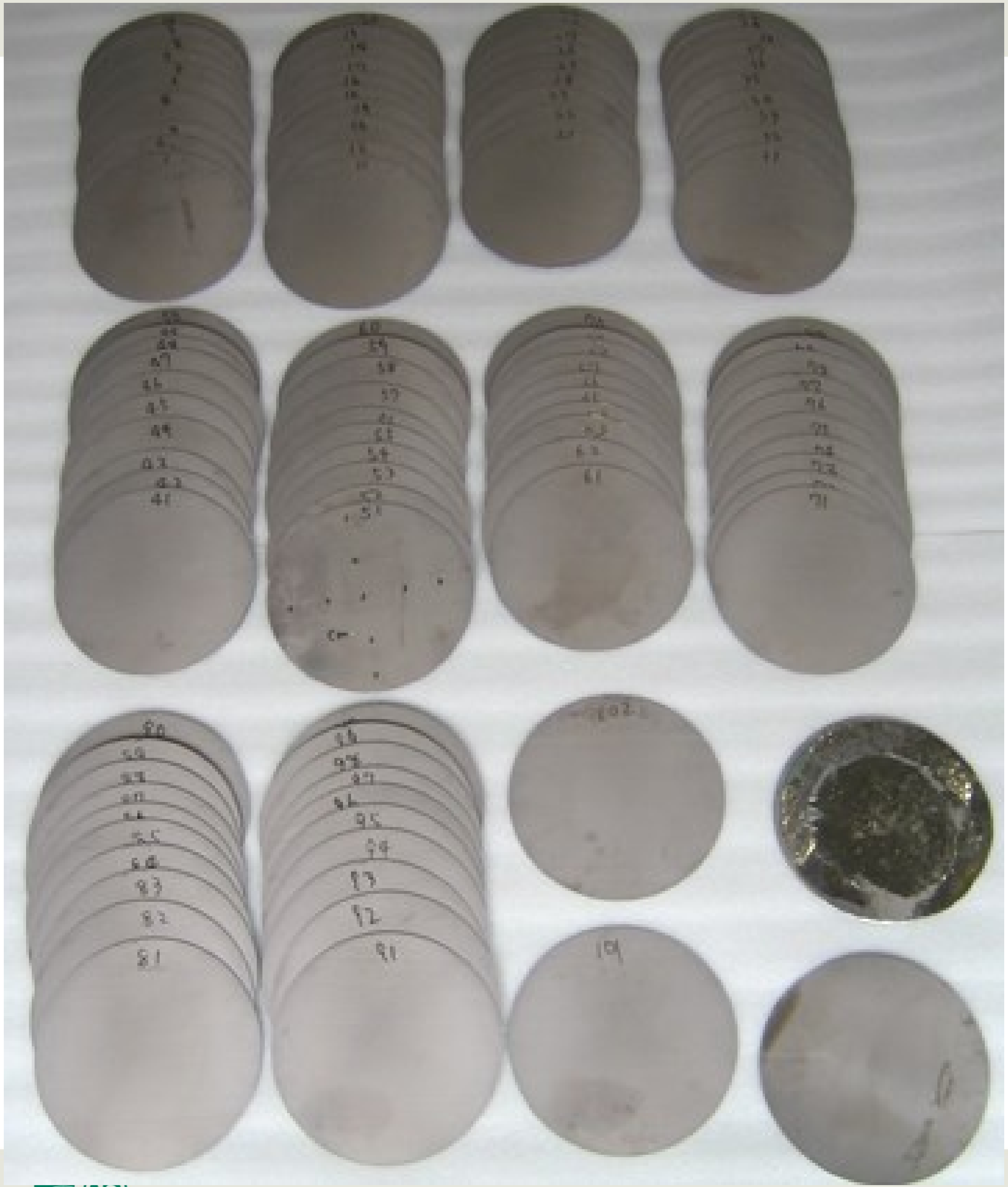
Slicing test up to 100 sheets







Sliced 102 Niobium Sheets for Cavity Fabrication

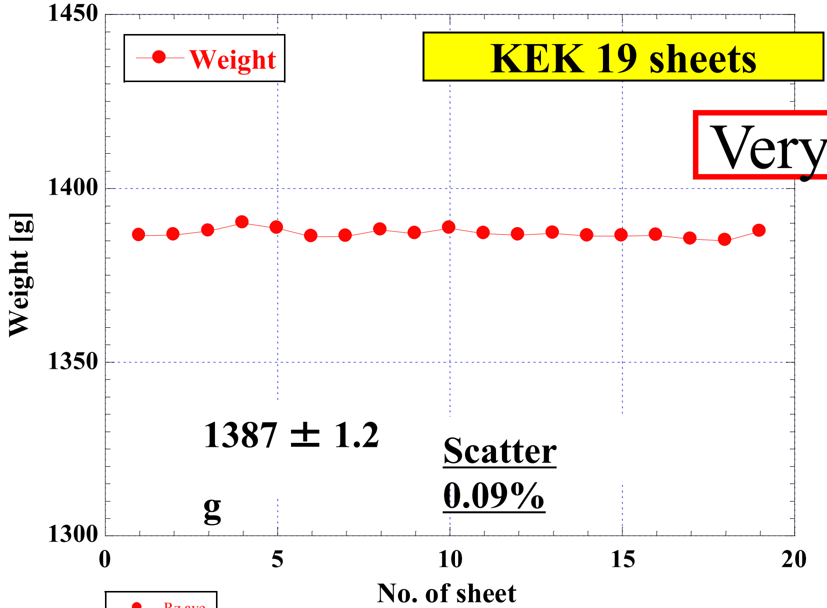


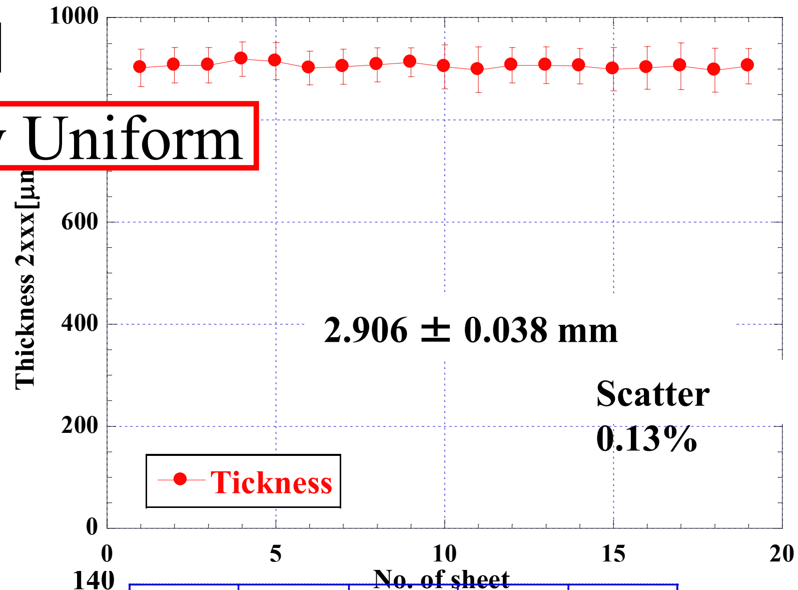
RRR reduction by this slicing is small, within the material variation.

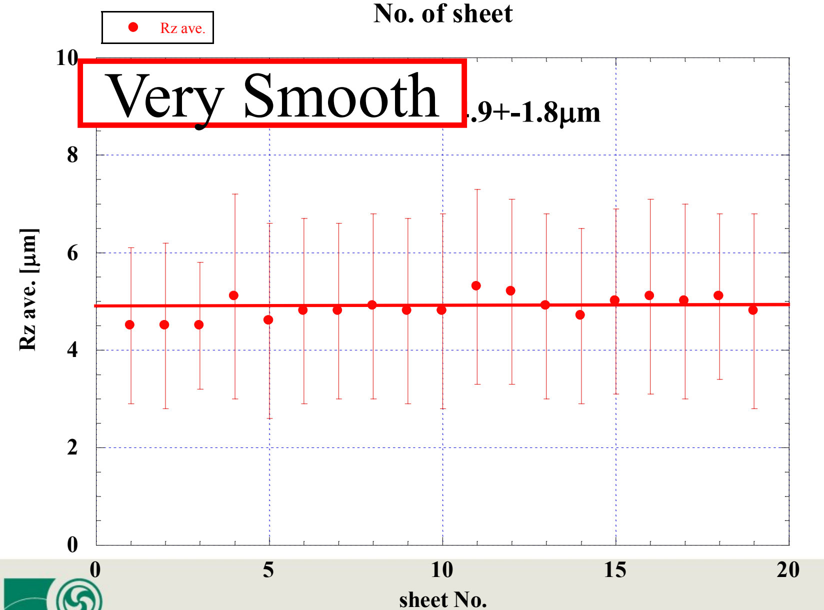
480 → 430

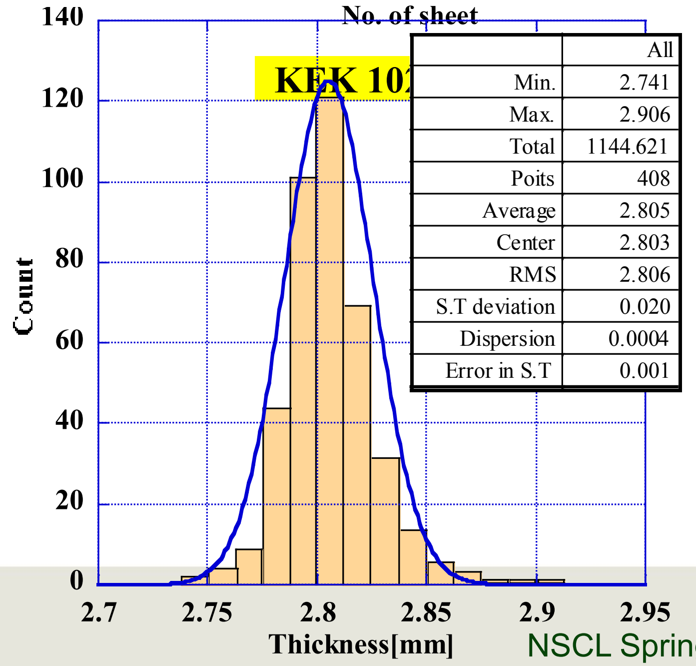
Degradation of RRR by this slicing is about 10% .

Feature of The Multi-Wire Slicing





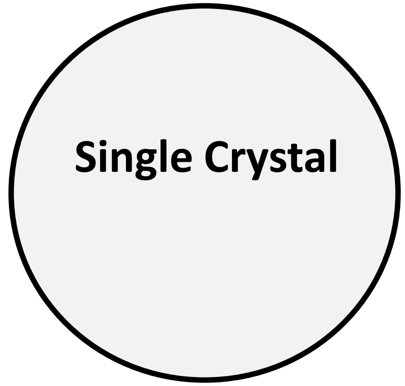


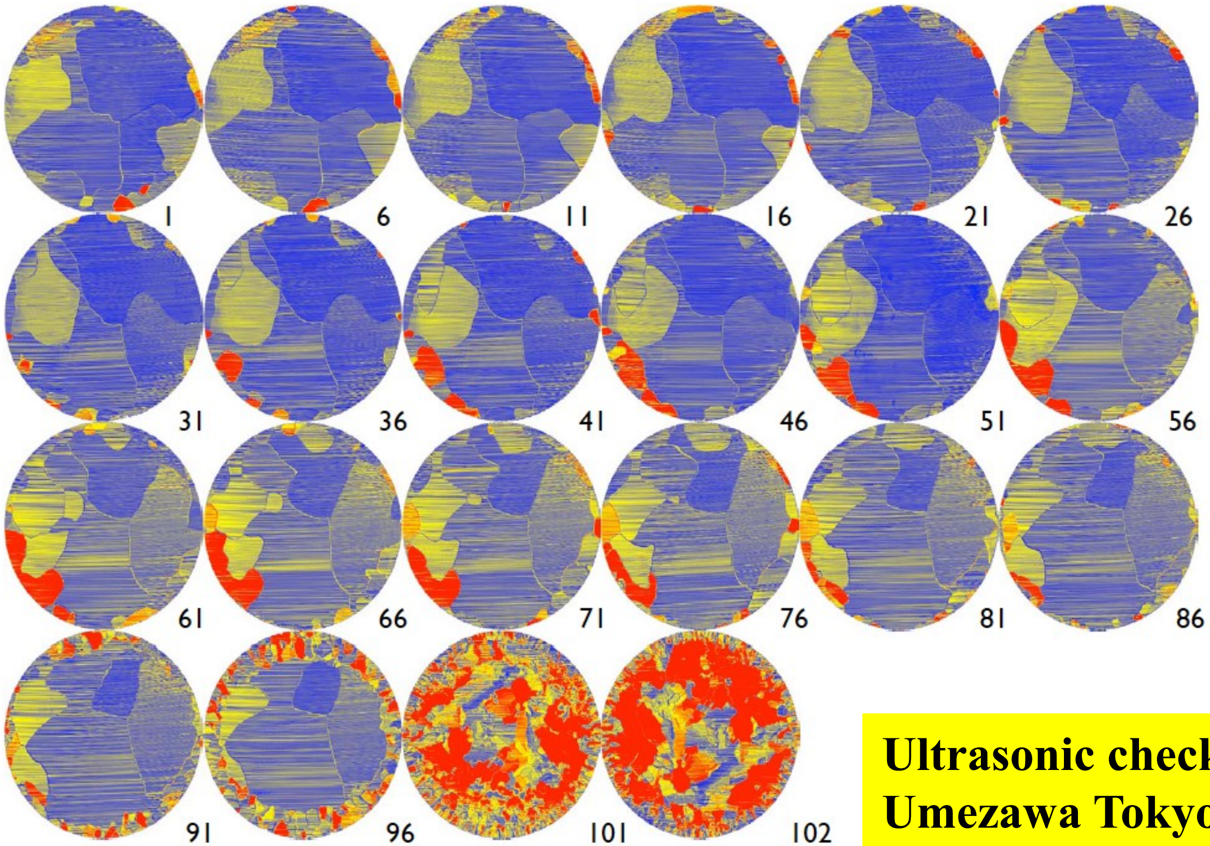


	All
Min.	2.741
Max.	2.906
Total	1144.621
Poits	408
Average	2.805
Center	2.803
RMS	2.806
S.T deviation	0.020
Dispersion	0.0004
Error in S.T	0.001

6.6 Approach for single crystal Nb ingot

Improvement of crystallization at Tokyo Denkai





Grains grow column likely by EBM.

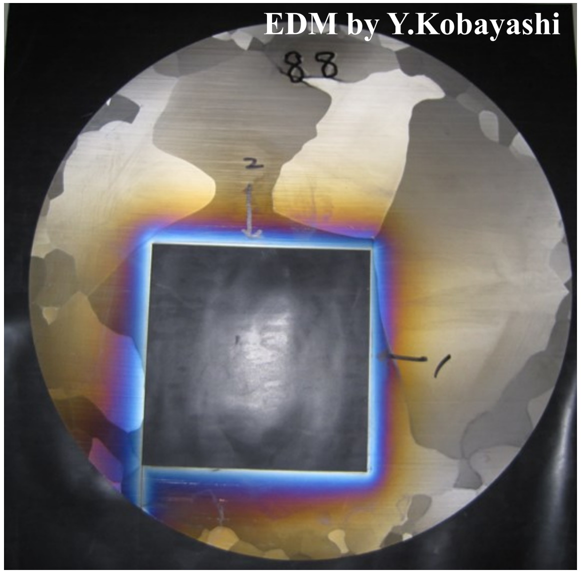
Make a seed with single crystal

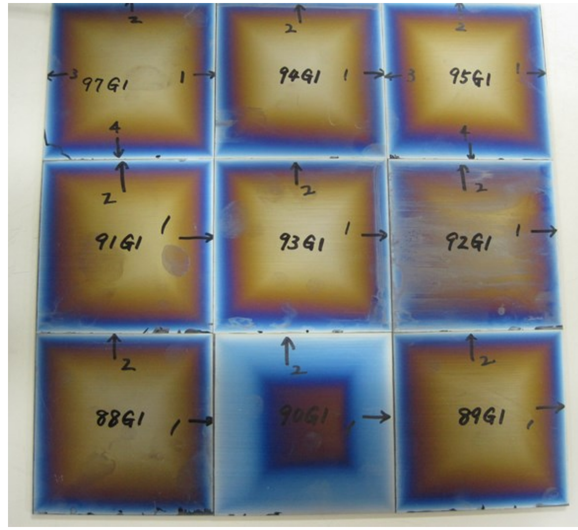
Ultrasonic check by Umezawa Tokyo-Denkai

Seed plate for EBM Nb Ingot

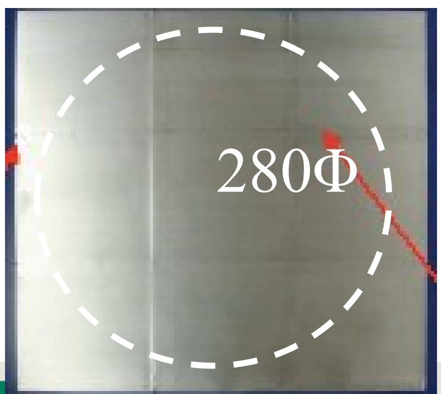
Use nearby 9 sheets

Cut out large crystal piece

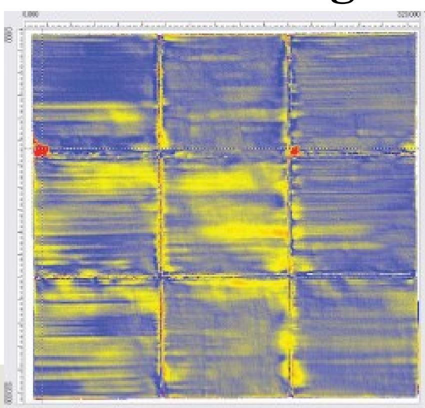




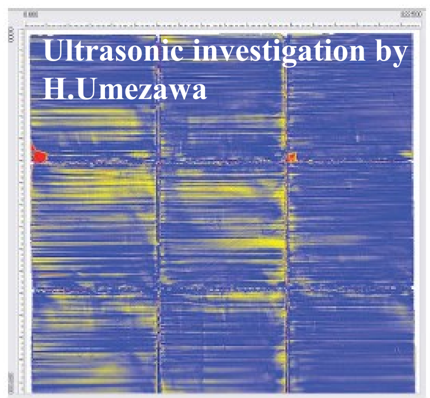
After BCP



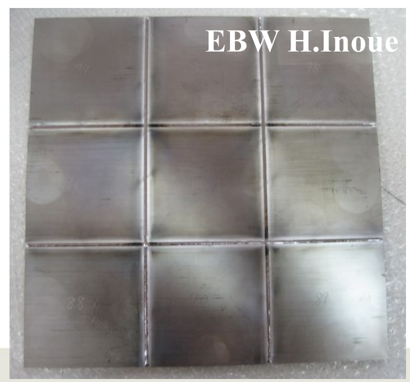
Ultrasonic diagnosis after buffing



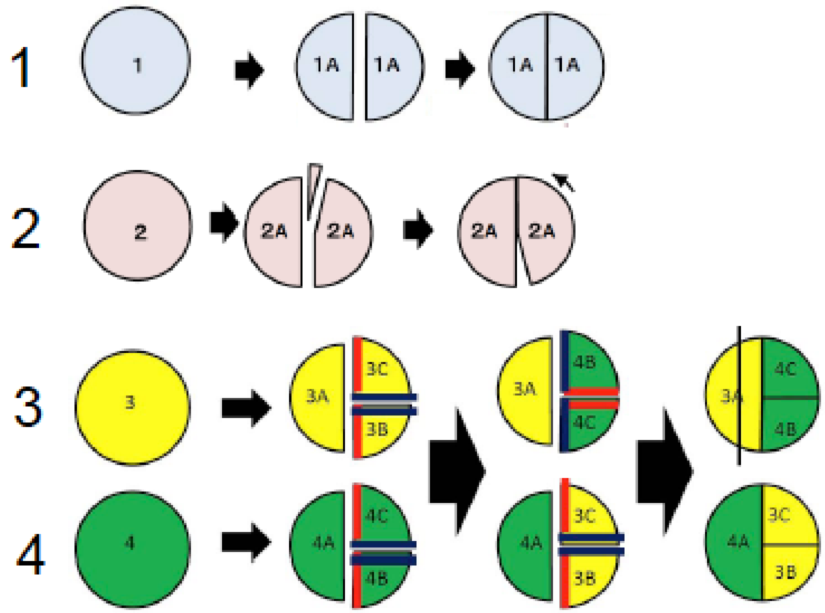
Ultrasonic diagnosis as received

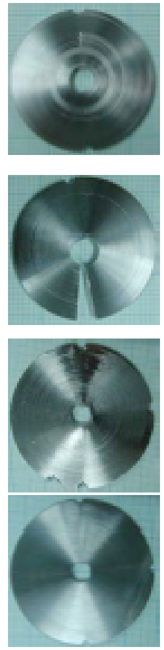


EBW of large crystal pieces



Mismatching Test





Grain Boundary?

No

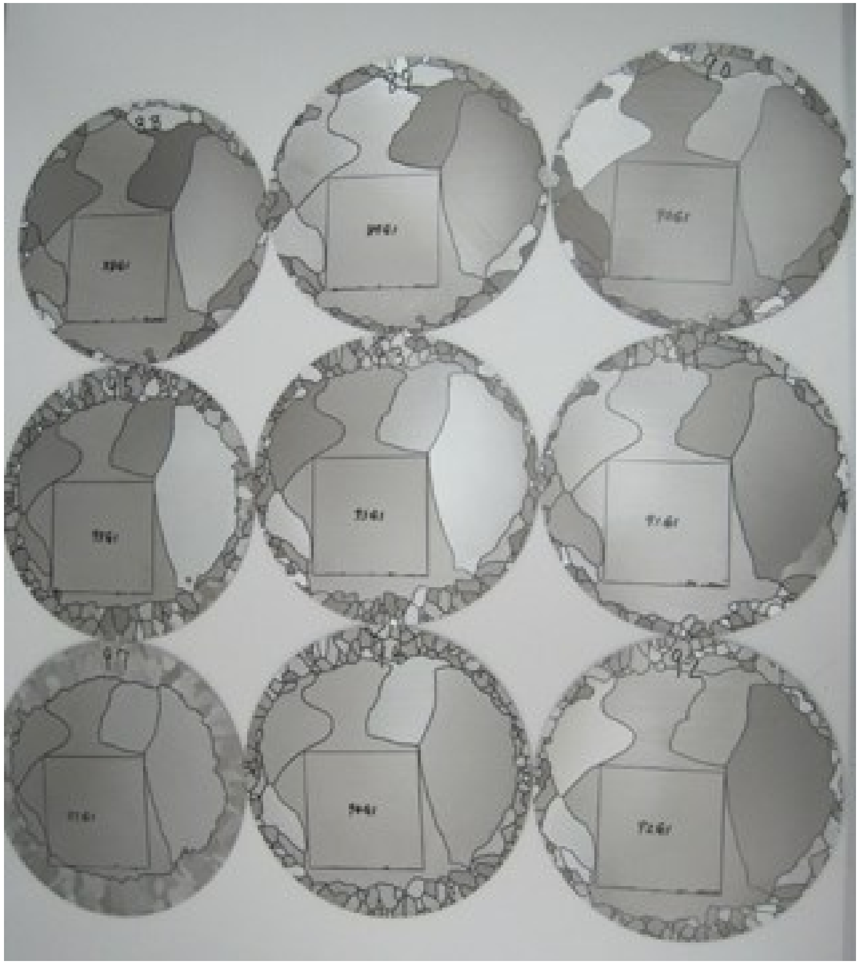
Yes

3A-(4C,4B) Yes
4C-4B Yes

4A-(3C,3B) Yes
3C-3B No

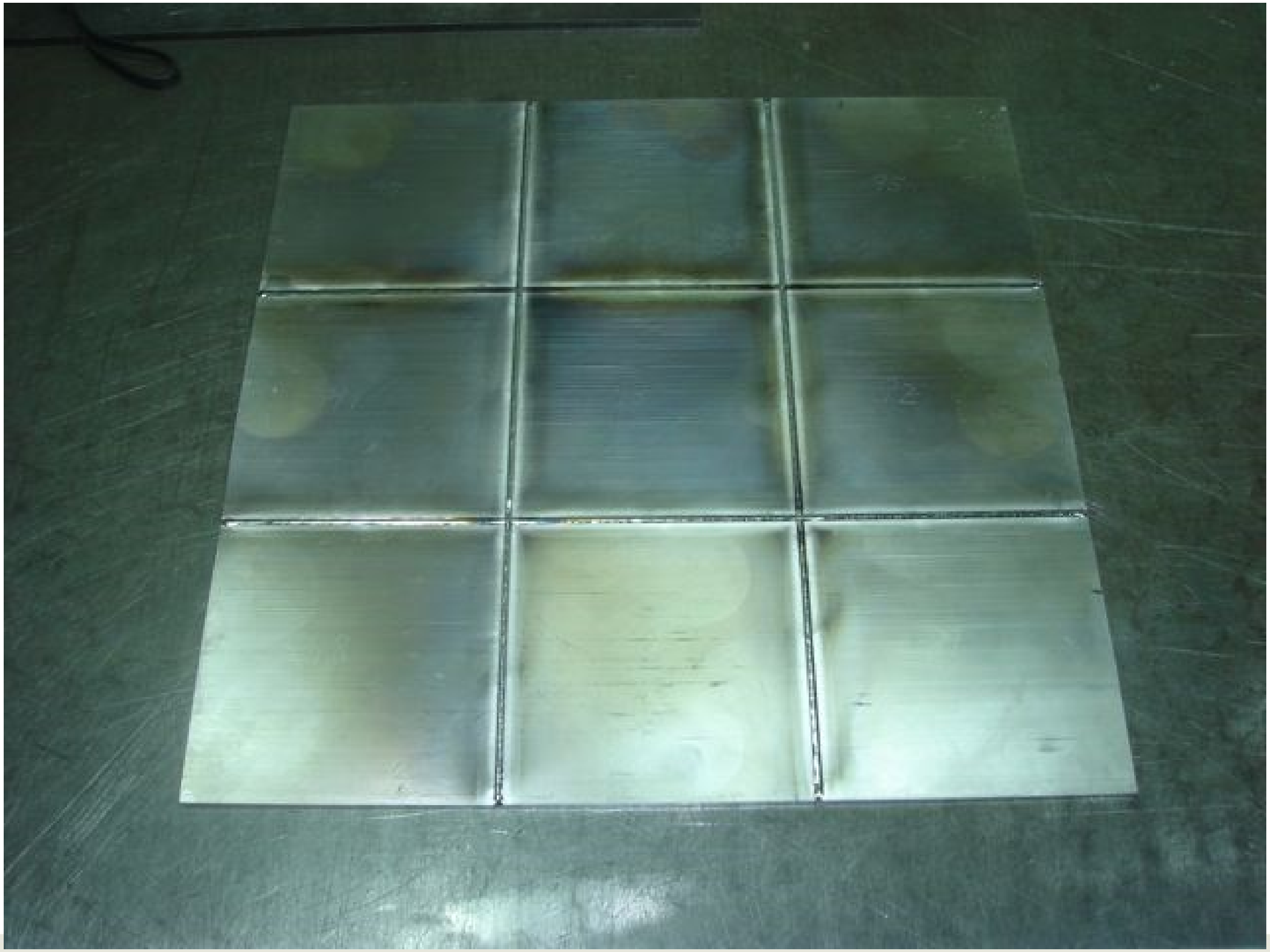
1. Each same crystals, doesn’t make a grain boundary (GB).
2. Even if same crystal, deferent angle make a GB.
3. Reveres side makes GB (i.e. angle is different). Weld Bead doesn’t make GB.
4. Same crystal, same direction doesn’t make GB

Cutting out LG-Nb Single crystal piece

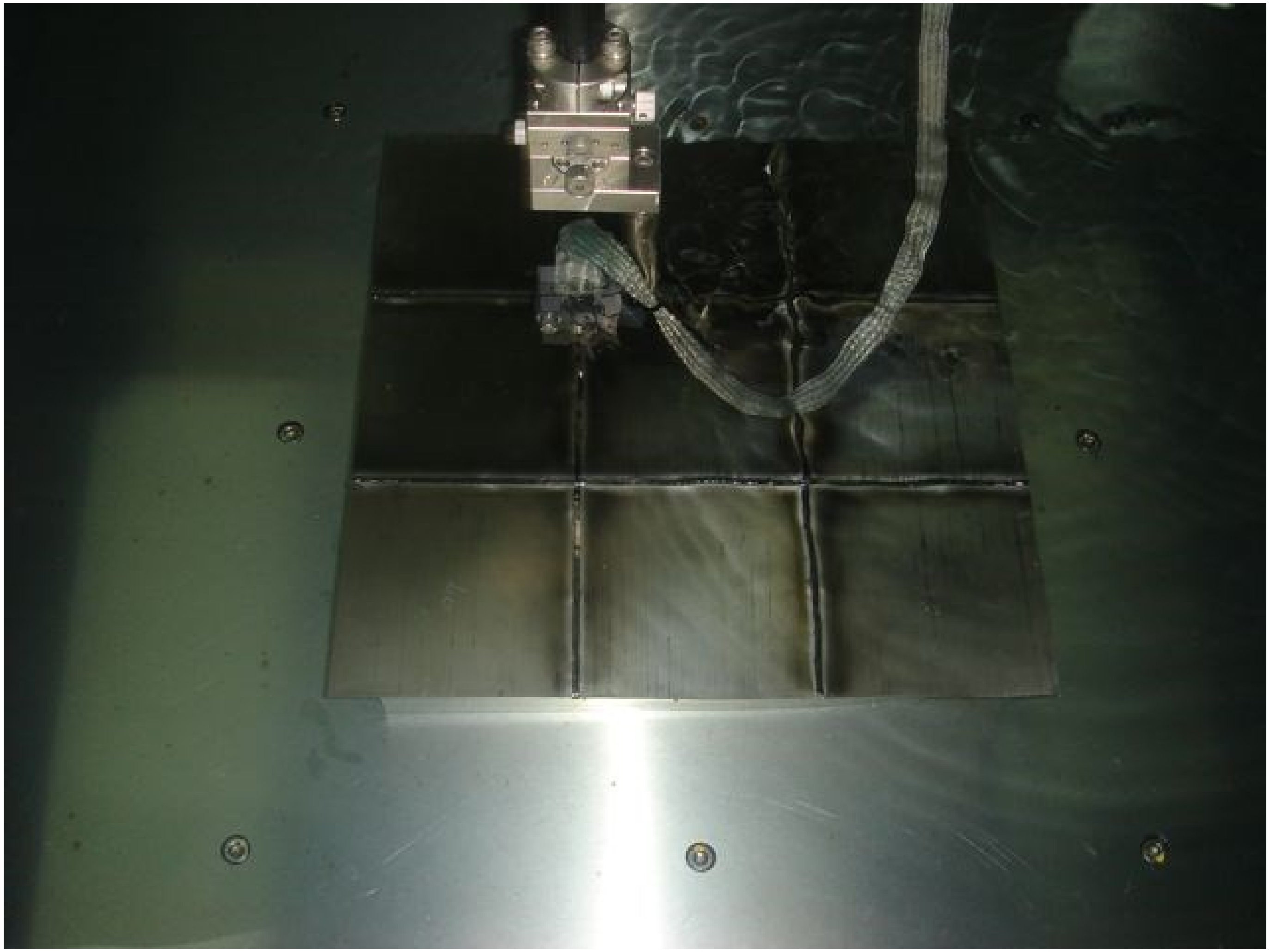


- **Cut out 9 single crystal parts from 9 large gran.**
- **The sheet size is 105 x 105mm square.**
- **EB welded together and produced 300 x 300 mm square sheet**

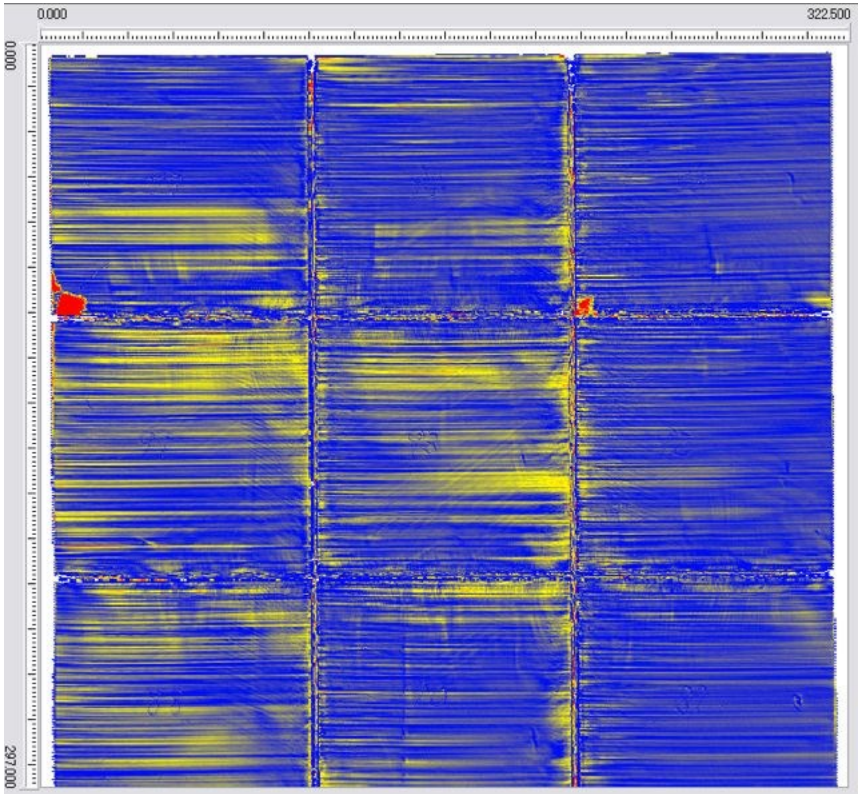
EB welded sheet



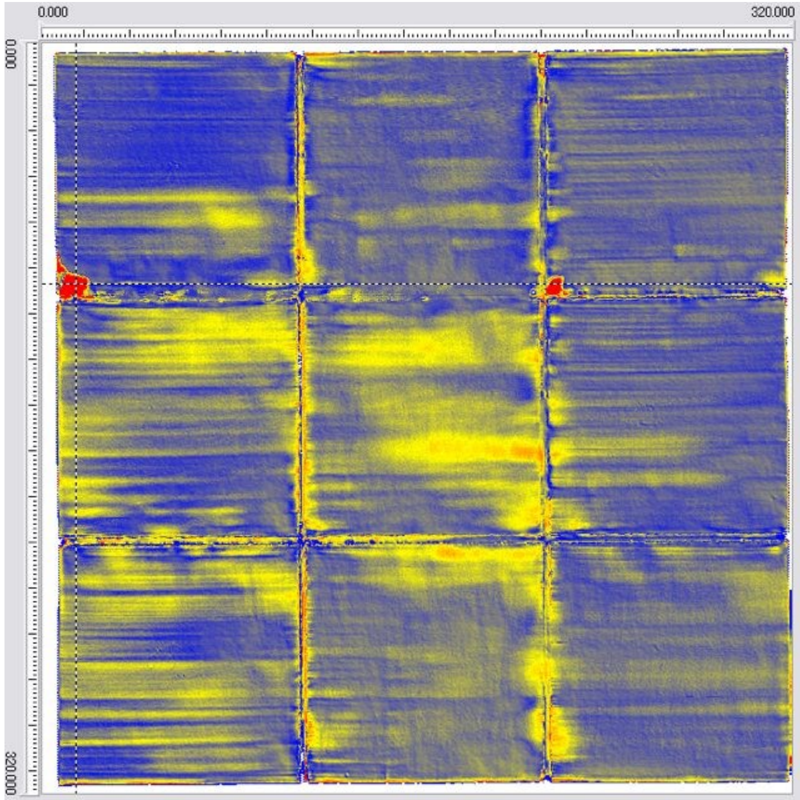
Ultrasound inspection in the water



Ultrasound inspection result



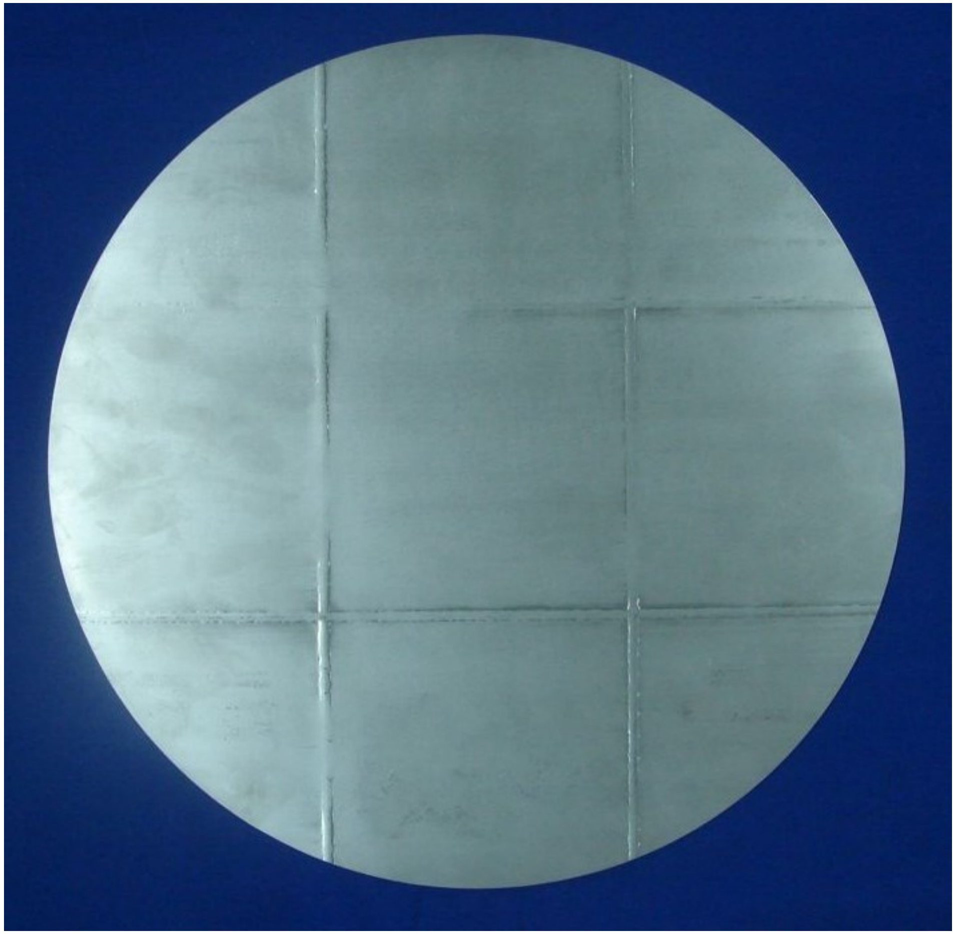
As Received
Observed wire sawing trace marks



After buffing and Buffered Chemical Polishing (BCP)
Observed non-uniformity in the thickness due to the buffing

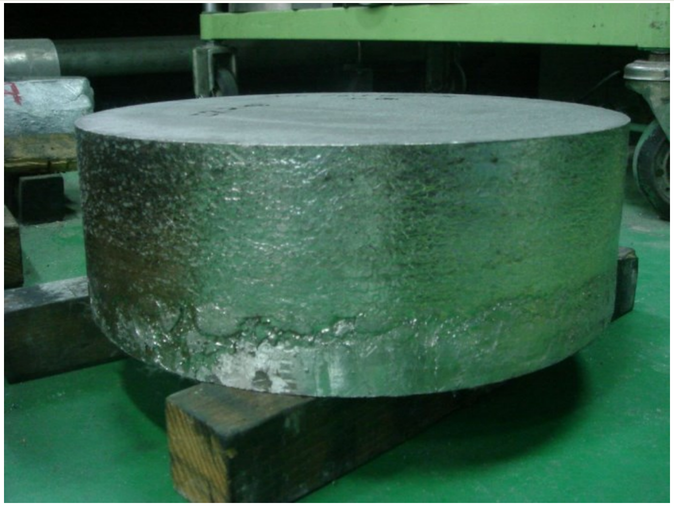
Observed grain boundary mismatches at two locations

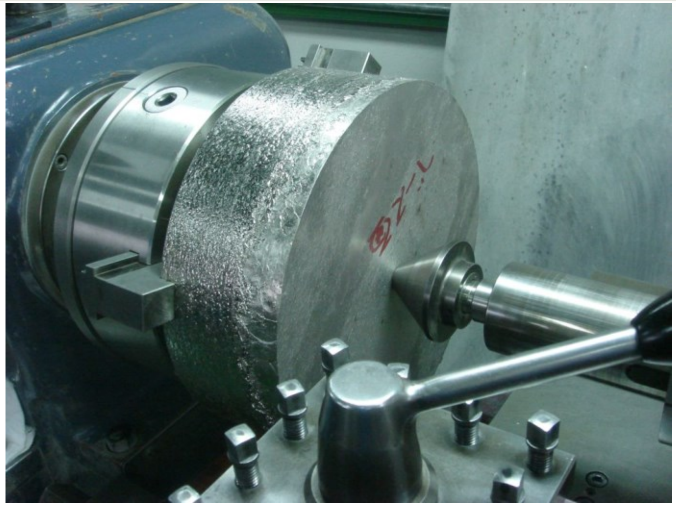
Completed single (not perfect) crystal seed plate

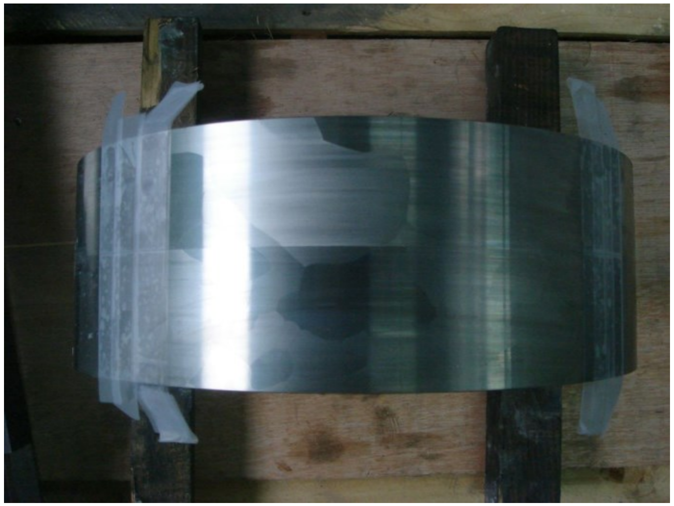


Single crystal sheet plate on the Nb seed

EB melted ingot on the crystal seed

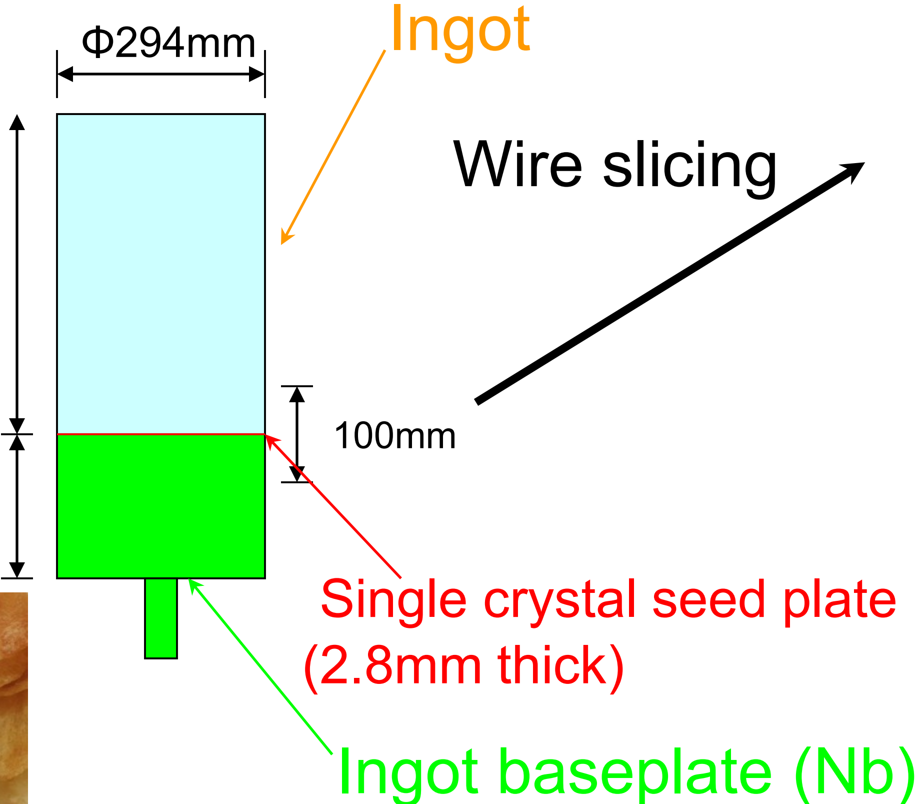


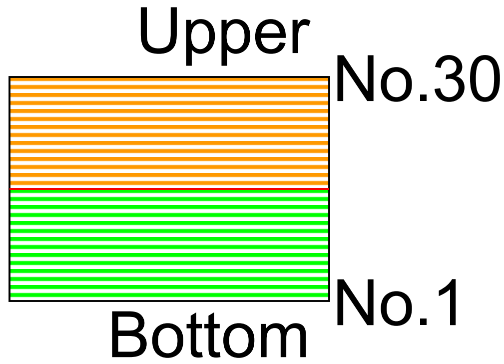




- Cutting the surface skin of the EB melted ingot.
- A clear boundary can be seen between the newly EB melted part and seed ingot.

Ingot slicing

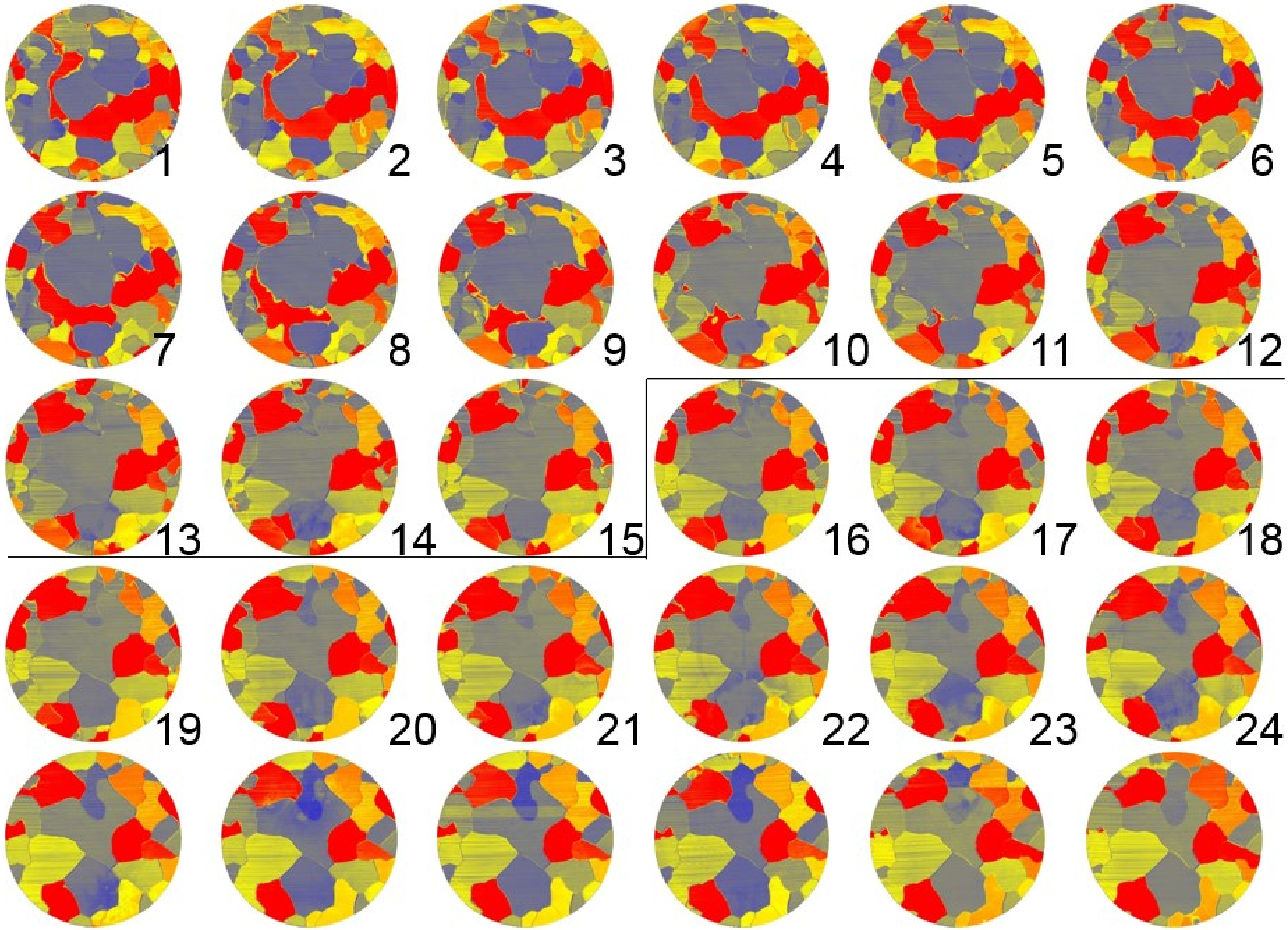




Sliced out 30 sheets with 2.8 mm thick
No.15 is closed to the crystal seed plate.

In this EB melting, the single crystal sheet became "potato-chips" shape at the first EB fitting, the single crystal seed was lost. Failed!!

Sheets wire sliced from the ingot



National Science Foundation
Michigan State University

Homework

- Homework 2

HW 2-1

Submit your report about how industrial niobium material was improved in the purity.

HW 2-2

Final residual metal contamination is Tantalum in niobium ingot.

If the residual is 100ppm, what is the theoretically highest expecting RRR for the niobium ingot?