# New Production Process of Nb Powder by Preform Reduction Process

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# Background

Miniaturization and high performance of mobile equipment

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Miniaturization and high capacity of electronic parts

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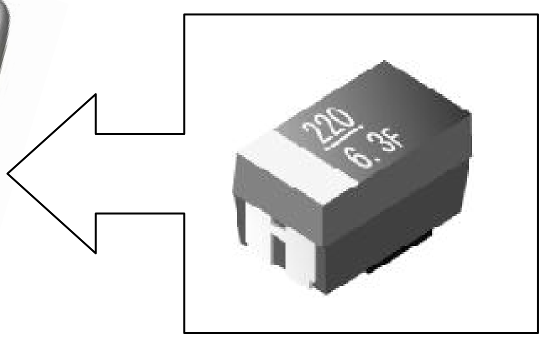
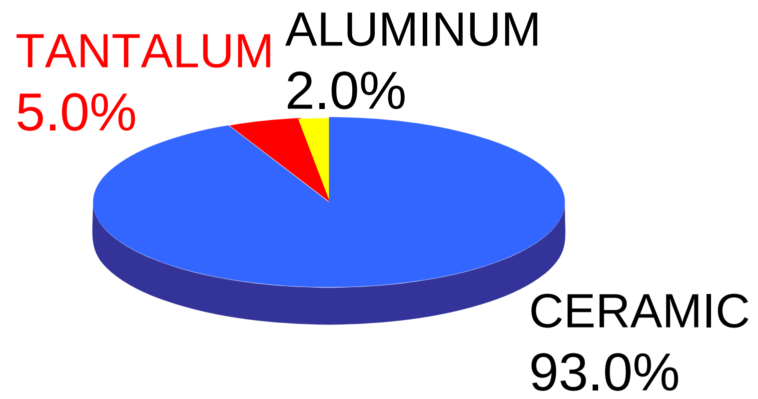
Demand of Ta capacitor is expanding.

- small
- high capacitance
- high thermal stability




Tantalum capacitor

(a) Quantity




(b) Cost

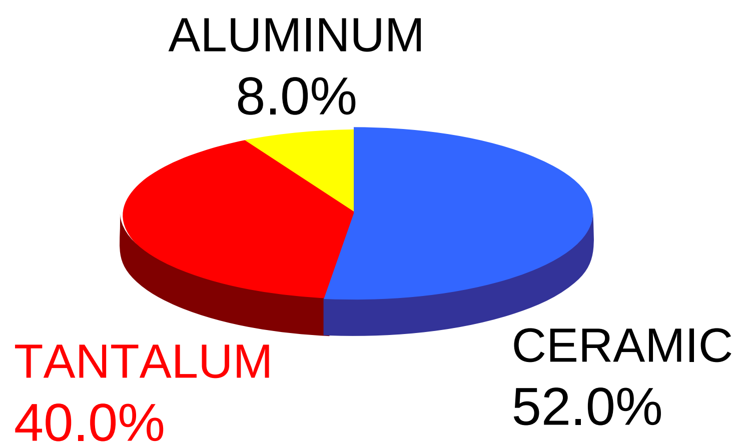



**Fig.** Market shares of capacitors in computer market.

Ref: Michael Lauri: “Capacitor Trends in the Computer Industry”, Proceedings of TIC Meeting 2000, Monday Oct. 23rd 2000 San Francisco, US.

# Comparison between Nb and Ta

| | Niobium | | Tantalum | |
|---|---|---|---|---|
| Symbol of element | Nb | | Ta | |
| Atomic number | 41 | | 73 | |
| Atomic weight | 92.9 | | 180.9 | |
| Density | 8.56 | $g/cm^3$ | 16.65 | $g/cm^3$ |
| Melting point | 2468 | ℃ | 2980 | ℃ |
| Boiling point | 4758 | ℃ | 5534 | ℃ |
| Resistivity(20℃) | 12.5 | Ω・cm | 12.4 | Ω・cm |
| Clarke number | $2 \times 10^{-3}$ (34th) | | $1 \times 10^{-3}$ (40th) | |
| World production | 23000 | ton | 2300 | ton |
| Demand in Japan | 3900 | ton | 550 | ton |
| Price (in round numbers) | 55 | $/kg | 700 | $/kg |

Nb with reference to Ta

Production volume : 10 times larger

Price : less than 1/10

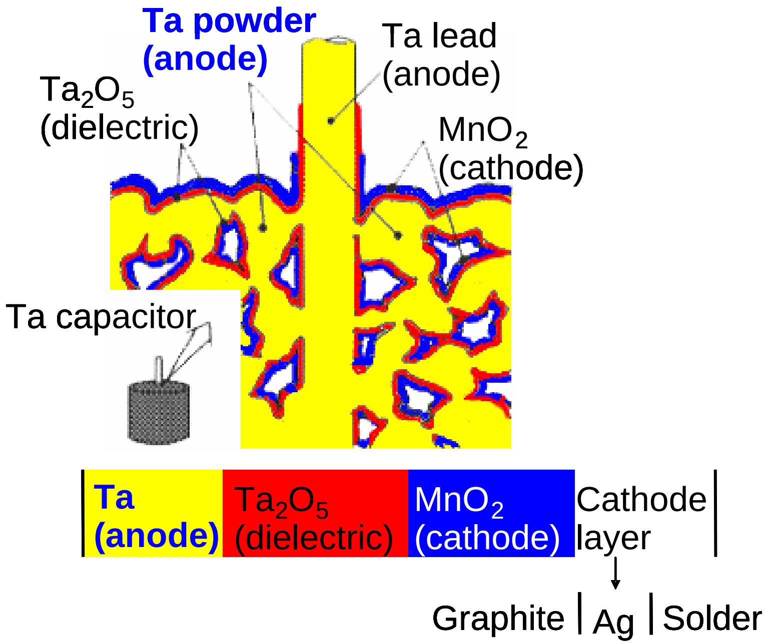
→ Nb is emerging as a material that can substitute for Ta in capacitors.

# Necessity for fine powder

Capacitance (C)

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot S}{d}$$

$C$ : capacitance
$\varepsilon_0$ : absolute permitivity of free space
$\varepsilon_r$ : relative permitivity of dielectric
$S$ : **specific surface area**
$d$ : plate distance (dielectric thickness)

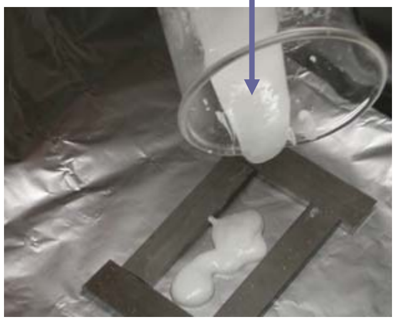



Higher specific surface area would result in higher capacitance.

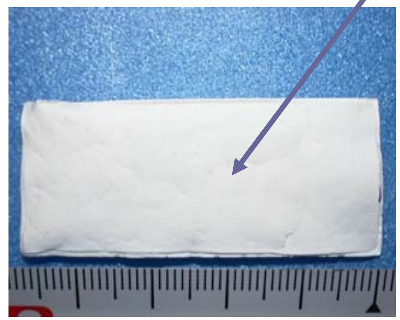
Fine particles are necessary to fabricate high-capacitance capacitor.

# Preform Reduction Process (PRP)

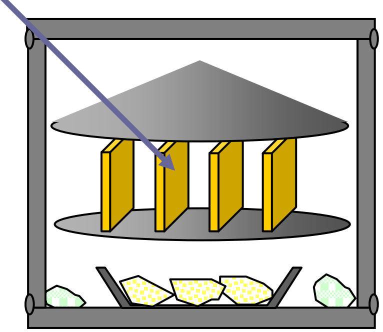
$Nb_2O_5$ + Flux + Binder → Preform



Casting



Forming



Reduction by Mg vapor

Chemical reaction:

$Nb_2O_5 + 5\,Mg \rightarrow 2\,Nb + 5\,MgO$

## ＜Features＞

- Fine and homogeneous powder obtainable
- No emission of waste solution containing fluorine
- Flexible scalability
- Small amount of molten salts required
- (semi-) Continuous and high-speed process

# Purpose of this study

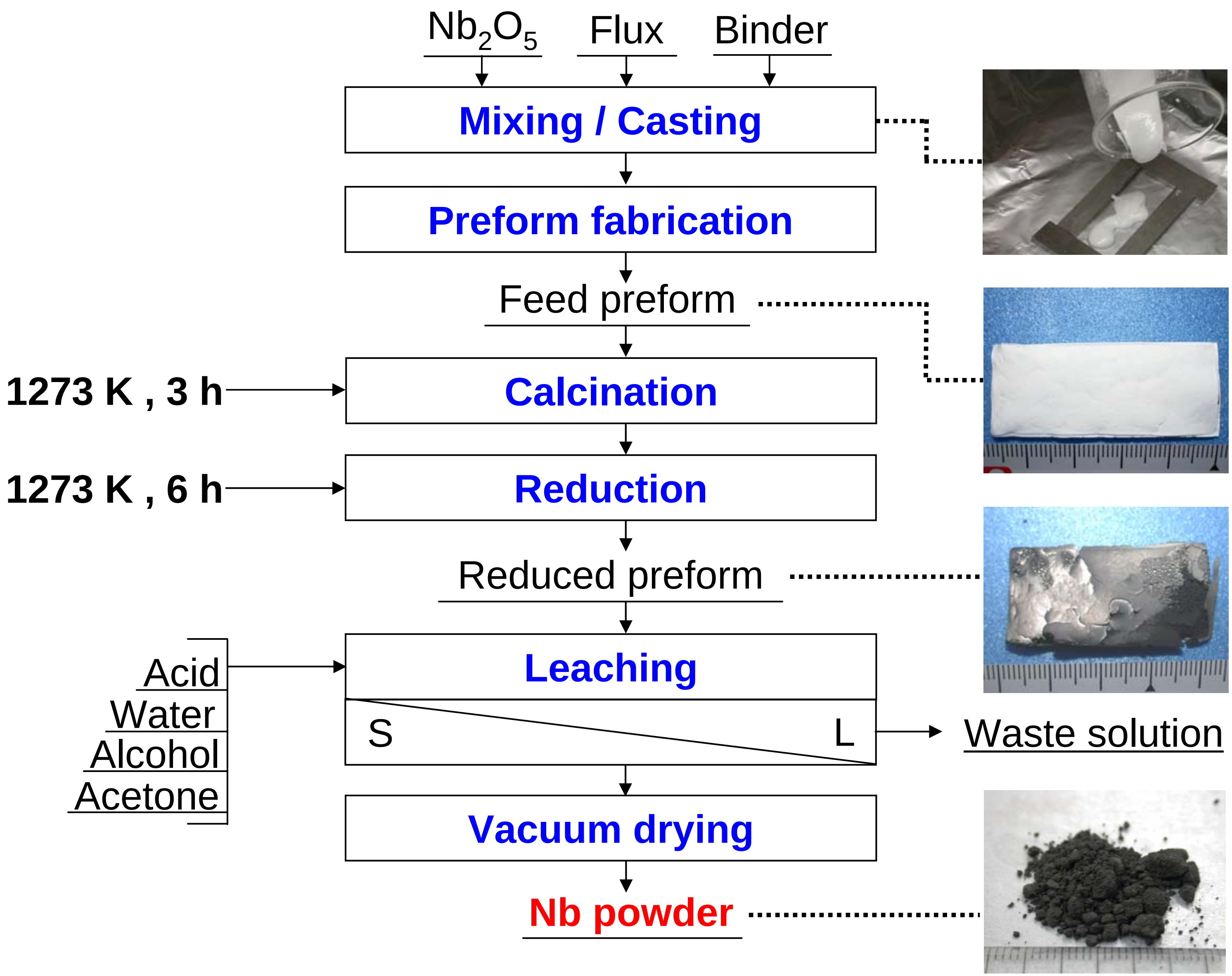
Production of fine Nb powder by using PRP

⇨ Influence of the vapor pressure of the reductant on the size and surface area of Nb particles

Investigation on new process for increasing the surface area of Nb powder

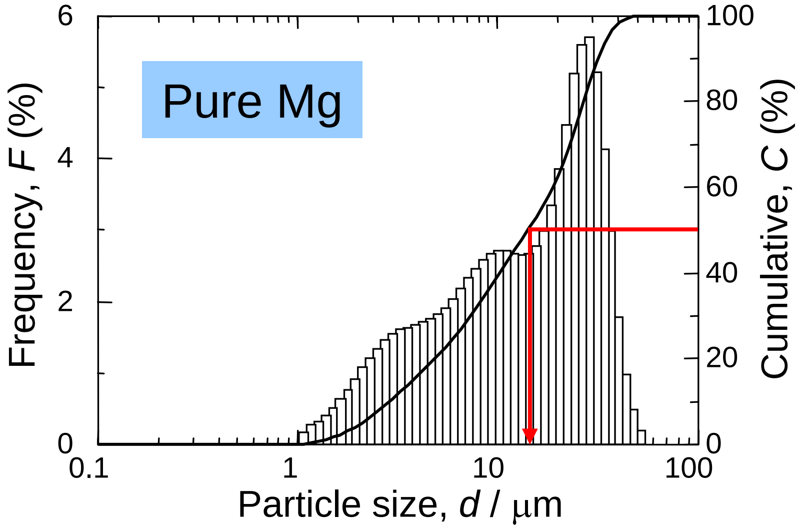
⇨ Alloying and dealloying treatment by metal vapor

# Flowchart of PRP

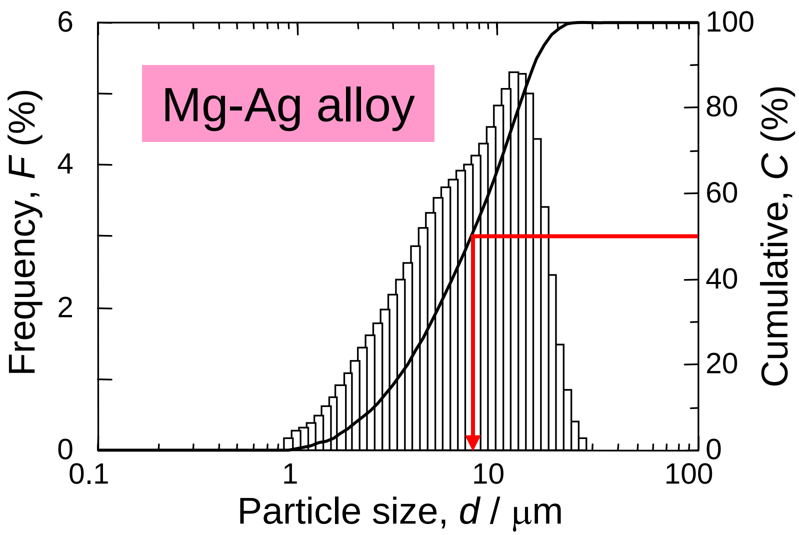


# Results （particle size distribution）

A




B

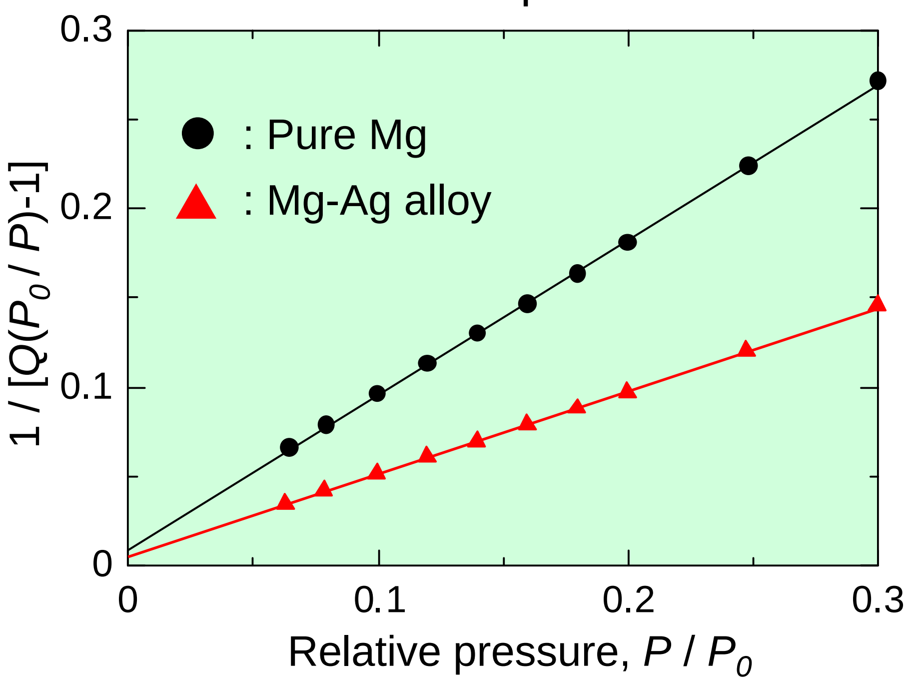



| Reductant, R | Particle size distribution | | |
|---|---|---|---|
| | $D_{10}$ / μm | $D_{50}$ / μm | $D_{90}$ / μm |
| Pure Mg | 2.91 | 14.13 | 31.46 |
| Mg-Ag alloy | 2.40 | 7.37 | 15.16 |

Particle size decreased when the Mg-Ag alloy was used as a reductant.

# Results (specific surface area measurement)

BET plot




$$\frac{1}{Q[(P_0/P)-1]} = \frac{C-1}{Q_m C}\left(\frac{P}{P_0}\right) + \frac{1}{Q_m C}$$

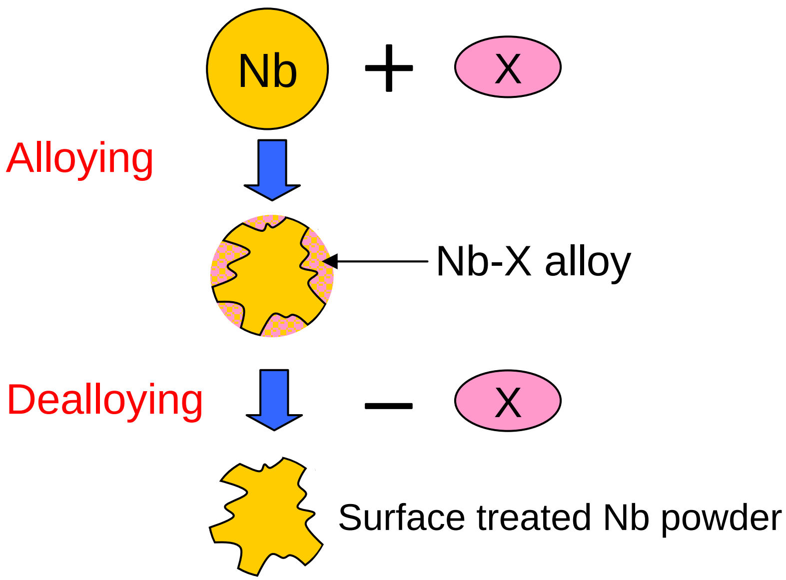
$P$ : equilibrium pressure of adsorption
$P_0$ : saturation pressure of gas
$Q$ : amount of adsorption at P
$Q_m$ : amount of monolayer adsorption
$C$ : BET constant

Mg vapor pressure in the reaction system was reduced by the alloying process, and the supply rate of Mg was suppressed.

| Reductant, R | Amount of monolayer adsorption, $Q_m$ | BET constant, $C$ | Specific surface area, $S$ / $m^2 \cdot g^{-1}$ |
|---|---|---|---|
| Pure Mg | 1.12 | 94.42 | 4.98 |
| Mg-Ag alloy | 2.12 | 98.81 | 9.21 |

Specific surface area increased when Mg-Ag alloy was used.

# Alloying and dealloying treatments




Nb powder + alloying element(X)

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Heating (alloying by X Vapor)

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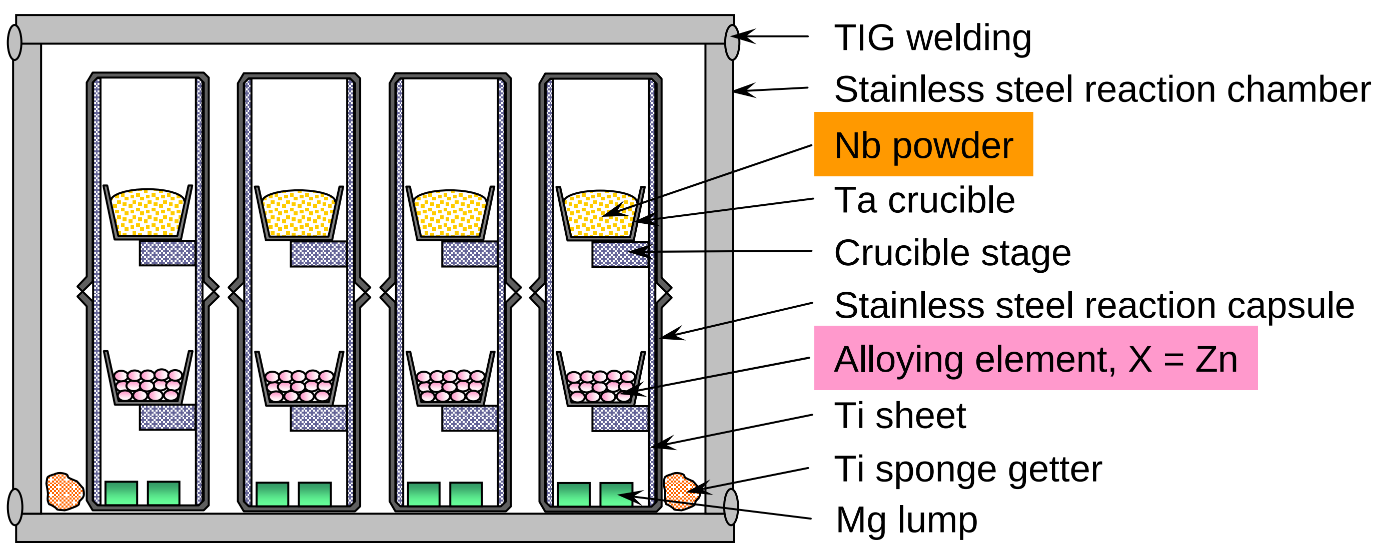
Acid dissolution (dealloying)



# Results

## XRF analysis

| | Concentration of element *i*, $C_i$ (mass%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Nb | Zn | Fe | Cr | Ni | Ti | Ta |
| after alloyng Zn | 76.0 | 23.65 | 0.06 | <0.01 | 0.02 | <0.01 | 0.22 |
| after acid dissolution | 99.6 | 0.05 | 0.02 | 0.03 | 0.03 | <0.01 | 0.23 |

Zn was dissolved and removed by leaching.

## Specific surface area measurement

| Sample | Specific surface area, $S$ / $m^2 \cdot g^{-1}$ Before treatment | | Specific surface area, $S$ / $m^2 \cdot g^{-1}$ After treatment |
|---|---|---|---|
| A | 1.61 | → | 2.65 |
| B | 7.25 | → | 7.28 |

When the Nb powder with low surface area was used as the starting material, the specific surface area of powder increased predominantly after the alloying and dealloying treatments.

# Summary

- Nb powder with high specific surface area and low particle size was obtained by PRP using Mg-Ag alloy as a reductant.
- Specific surface area of Nb powder was increased by alloying with Zn vapor and dealloying with acid.

# Future work

Search for higher specific surface area at dealloying treatment

・More efficient wet process

・Vacuum distillation

・Use of Mn or other metals as an alloying element

→ Simultaneous process for preform reduction and alloying

Thank you very much.