New Production Process of Nb Powder by Preform Reduction Process

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Background

Miniaturization and high performance of mobile equipment

Miniaturization and high capacity of electronic parts

Demand of Ta capacitor is expanding.
- small
- high capacitance
- high thermal stability

(a) Quantity

<table>
<thead>
<tr>
<th>Capacitor Type</th>
<th>Market Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>TANTALUM</td>
<td>5.0%</td>
</tr>
<tr>
<td>ALUMINUM</td>
<td>2.0%</td>
</tr>
<tr>
<td>CERAMIC</td>
<td>93.0%</td>
</tr>
</tbody>
</table>

(b) Cost

<table>
<thead>
<tr>
<th>Capacitor Type</th>
<th>Market Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALUMINUM</td>
<td>8.0%</td>
</tr>
<tr>
<td>TANTALUM</td>
<td>40.0%</td>
</tr>
<tr>
<td>CERAMIC</td>
<td>52.0%</td>
</tr>
</tbody>
</table>

Fig. Market share of capacitors in computer market.
### Comparison between Nb and Ta

<table>
<thead>
<tr>
<th></th>
<th>Niobium</th>
<th>Tantalum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol of element</td>
<td>Nb</td>
<td>Ta</td>
</tr>
<tr>
<td>Atomic number</td>
<td>41</td>
<td>73</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>92.9 g/cm³</td>
<td>180.9 g/cm³</td>
</tr>
<tr>
<td>Density</td>
<td>8.56 g/cm³</td>
<td>16.65 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>2468 °C</td>
<td>2980 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>4758 °C</td>
<td>5534 °C</td>
</tr>
<tr>
<td>Resistivity(20°C)</td>
<td>12.5 Ω·cm</td>
<td>12.4 Ω·cm</td>
</tr>
<tr>
<td>Clarke number</td>
<td>2 × 10⁻³ (34th)</td>
<td>1 × 10⁻³ (40th)</td>
</tr>
<tr>
<td>World production</td>
<td>23000 ton</td>
<td>2300 ton</td>
</tr>
<tr>
<td>Demand in Japan</td>
<td>3900 ton</td>
<td>550 ton</td>
</tr>
<tr>
<td>Price (in round numbers)</td>
<td>55 $/kg</td>
<td>700 $/kg</td>
</tr>
</tbody>
</table>

Nb with reference to Ta
- Production volume: 10 times larger
- Price: less than 1/10

Nb is emerging as a substitute material of Ta for use in capacitor.
Necessity for fine powder

Capacitance (C)

\[ C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot S}{d} \]

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

High specific surface area leads to high capacitance.

Fine particle is necessary to produce high-capacitance capacitor.
Preform Reduction Process (PRP)

\[ \text{Nb}_2\text{O}_5 + 5 \text{Mg} \rightarrow 2 \text{Nb} + 5 \text{MgO} \]

**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 PRP

- Influence of vapor pressure of reductant on Nb particle size and surface area

Investigation on new process for increasing surface area of Nb powder

- Alloying and dealloying treatment by metal vapor
Flowchart of PRP

1. Mixing / Casting
2. Preform fabrication
3. Mixing / Casting
4. Feed preform
5. Calcination
   - 1273 K, 3 h
6. Reduction
   - 1273 K, 6 h
7. Reduced preform
8. Leaching
   - Acid
   - Water
   - Alcohol
   - Acetone
   - LS
   - S
   - L
   - Waste solution
9. Vacuum drying
10. Nb powder

Materials:
- Nb₂O₅
- Flux
- Binder

Steps:
- Nb₂O₅
- Flux
- Binder
- Nb powder
Results (particle size distribution)

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

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{10}$ / μm</td>
</tr>
<tr>
<td>Pure Mg</td>
<td>2.91</td>
</tr>
<tr>
<td>Mg-Ag alloy</td>
<td>2.40</td>
</tr>
</tbody>
</table>

- Pure Mg
- Mg-Ag alloy
Results  (specific surface area measurement)

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

- \( P \) : 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 decreased by alloying, and supply rate of Mg was suppressed.

Specific surface area was increased by using Mg-Ag alloy.

<table>
<thead>
<tr>
<th>Reductant, ( R )</th>
<th>Amount of monolayer adsorption, ( Q_m )</th>
<th>BET constant, ( C )</th>
<th>Specific surface area, ( S / \text{m}^2 \cdot \text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>1.12</td>
<td>94.42</td>
<td>4.98</td>
</tr>
<tr>
<td>Mg-Ag alloy</td>
<td>2.12</td>
<td>98.81</td>
<td>9.21</td>
</tr>
</tbody>
</table>
Alloying and dealloying treatments

**Alloying**

- Nb powder + alloying element (X)
- Nb-X alloy

**Dealloying**

- Surface treated Nb powder
- Acid dissolution (dealloying)

**Equipment**

- TIG welding
- Stainless steel reaction chamber
- Nb powder
- Ta crucible
- Crucible stage
- Stainless steel reaction capsule
- Alloying element, X = Zn
- Ti sheet
- Ti sponge getter
- Mg lump

**Process**

- Heating (alloying by X Vapor)
- Acid dissolution (dealloying)
Results

XRF analysis

<table>
<thead>
<tr>
<th>Concentration of element $i$, $C_i$ (mass%)</th>
<th>Nb</th>
<th>Zn</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>after Zn alloying</td>
<td>76.0</td>
<td>23.7</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>after acid dissolution</td>
<td>99.6</td>
<td>0.05</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Zn was dissolved and removed by leaching.

Specific surface area measurement

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area, $S / m^2 \cdot g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before treatment</td>
</tr>
<tr>
<td>A</td>
<td>1.61</td>
</tr>
<tr>
<td>B</td>
<td>7.25</td>
</tr>
</tbody>
</table>

When Nb powder with low surface area was used as a starting material, specific surface area of powder was increased 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 Zn vapor alloying and acid dealloying treatment.

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