RECYCLING PROCESS FOR TANTALUM AND SOME OTHER METAL SCRAPS

Ryosuke Matsuoka¹, Kunio Mineta¹, Toru H. Okabe²

¹Graduate student, Graduate School of Engineering, University of Tokyo, Tokyo, Japan

²Institute of Industrial Science, University of Tokyo, Tokyo, Japan
Introduction

Features of Ta capacitor

1. Largest capacity per unit volume among capacitors.
2. High thermal stability

Demand for small sized high-performance electric devices increased in the last 10 years

Demand for Ta capacitor is accelerated.

Fig. The market share of capacitors in a certain computer market\(^1\).

Purpose of this research

- Large amount of off-spec Ta capacitors are generated during the manufacturing process.

- No effective recycling process (Actually scraps are treated as Ta ore) Ta capacitor scraps are high quality Ta resource which do not contain any Nb.

Ta recycling is important from the view point of resource preservation, minimization of waste materials, and saving energy for recycling.

Objective of this research

Development of an effective process for Ta recovery from capacitor scraps.
Structure of Ta capacitor

- **Fireproof epoxy resin**
  Polymer including SiO₂

- **Sintered Ta electrode**
  Content of Ta is 90 mass% or higher.

- **Terminal**
  Fe, Ni, Cu...

Fig. Schematic illustration of tantalum capacitor.

Ta exists in the sintered Ta electrode

Separation of sintered electrode out of the scrap is important issue

Epoxy resin  Terminal

Removing external epoxy resin

Sintered Ta electrode in the capacitor
Ta recovery process

Investigated Mineta and Okabe. *1

Ta capacitor scrap

O₂ → **Oxidation** → CO₂, H₂O etc.

TaOₓ, SiOₓ, MgxOₓ

Magnetic separation → Fe, Ni

TaOₓ, SiOₓ, MgxOₓ

Water → **Sieving / Flushing**

S L → Waste solution

TaOₓ, MgxOₓ → SiOₓ etc.

Pulverizing / Sieving → MgxOₓ

TaOₓ, MgxOₓ

HNO₃ aq. → **Leaching**

S L → Waste solution

TaOₓ

Mg → **Reduction**

Ta, MgO, Mg

Acid → **Leaching**

S L → Waste solution

Ta

Fig. Flowchart of the recovery process for tantalum from capacitor scraps.

*1) K. Mineta and T. H. Okabe:
“Development of a Recycling Process for Tantalum from capacitor Scraps,”
International IUPAC Conference on High Temperature Materials Chemistry -XI Abstract,
Tokyo, Japan, 19-23 May (2003), 150.
Results of the recovery process

![XRD pattern](image1.png)

Fig. (a) XRD pattern of tantalum recovered from capacitor scraps, and (b) reference pattern of tantalum reported by JCPDS.

![SEM image](image2.png)

Fig. SEM image of Ta recovered from capacitor scraps.

### Table
Analytical result of tantalum powder recovered from tantalum capacitor scraps determined by ICP-AES analysis. The parenthetic data is estimated value.

<table>
<thead>
<tr>
<th>Concentration of element ( i ), ( C_i ) (mass %)</th>
<th>Ta</th>
<th>Si</th>
<th>Cu</th>
<th>Ag</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitor scrap</td>
<td>(40 ~ 50)</td>
<td>(10 ~ 20)</td>
<td>(~ 5)</td>
<td>(-)</td>
<td>(5 ~ 10)</td>
<td>(-)</td>
</tr>
<tr>
<td>Recovered ( \text{TaO}_x )</td>
<td>(80)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>Obtained Ta powder</td>
<td><strong>98.57</strong></td>
<td><strong>0.93</strong></td>
<td>0.07</td>
<td>0.16</td>
<td>0.25</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**1: Value determined by balancing the analyzed solute concentration.

- After reduction, **99 % purity of Ta** was obtained.
- The yield of the process was **90 ~ 92 %**.

Further Ta purification process is required, for use in electronic industry.

Chlorination reaction using chloride scraps from the Kroll process
Wastes from the Kroll process

Kroll process: Ti production process

Chlorination: Chlorination of Ti ore
\[ \text{TiO}_2 (+ \text{FeO}_x) + \text{C} + 2 \text{Cl}_2 \rightarrow \text{TiCl}_4 (+ \text{FeCl}_x) + \text{CO}_2 \]

Reduction: Reduction of TiCl\(_4\) using Mg
\[ \text{TiCl}_4 + 2 \text{Mg} \rightarrow \text{Ti} + 2 \text{MgCl}_2 \]

Electrolysis: Electrolysis of MgCl\(_2\)
\[ \text{MgCl}_2 \rightarrow \text{Mg} + \text{Cl}_2 \]

Upgrading Ti ore for minimizing chloride wastes

Large amount of chloride wastes (e.g. FeCl\(_x\)) are produced in the Kroll process.

Importance

1. Reduction of disposal cost of chloride wastes
2. Minimizing chlorine loss in the Kroll process
3. Improvement of environmental burden
Refining process using FeClᵥ

\[ \text{Ta} + \text{FeCl}_x \rightarrow \text{TaCl}_x + \text{Fe} \]
\[ \text{Ta}_2\text{O}_5 + \text{FeCl}_x + \text{C} \rightarrow \text{TaCl}_x + \text{Fe} + \text{CO} \]

Advantages:
1. Utilizing chloride wastes from Kroll process
2. Low cost Ta chlorination
3. Minimizing chlorine loss in the Kroll process caused by generation of chloride wastes

Effective utilization of chloride wastes

Development of a new environmentally sound chloride metallurgy
Thermodynamic analysis (chlorination)

When C or CO is introduced in the system, chlorination of Ta₂O₅ proceeds and TaCl₅ (g) generates under high Cl₂ partial pressure.

Fig. Chemical potential diagram for Ta-Cl-O system under constant chlorine partial pressure.
Fig. Vapor pressure of the chlorides of iron, tantalum, and silicon as a function of reciprocal temperature.

The separation of chlorides and the recovery of high-purity TaCl$_5$ (g) is possible by controlling deposition temperature.
Thermodynamic analysis (Ta chlorination)

Fig. Isothermal chemical potential diagram for Ta-Cl-O system at 900 K.

Chlorination of Ta<sub>2</sub>O<sub>5</sub> proceeds, when C or CO is introduced in the system.

Although Ta<sub>2</sub>O<sub>5</sub> is stable under Fe / FeCl<sub>2</sub> equilibrium, chlorination of Ta<sub>2</sub>O<sub>5</sub> may proceed by reducing total pressure, because vapor pressure of TaCl<sub>5</sub> is high.
Chlorination of Ta

\[ 2 \text{Ta} \,(s) + 5 \text{FeCl}_2 \,(s,g) = 2 \text{TaCl}_5 \,(g) + 5 \text{Fe} \,(s) \]
(or Fe$_2$Ta \,(s))

**TaCl$_5$ can be generated by reacting Ta and FeCl$_2$ or FeCl$_3$.**
Chlorination of Ta using FeCl₂

\[ 2 \text{Ta} (s) + 5 \text{FeCl}_2 (s) = 2 \text{TaCl}_5 (g) + 5 \text{Fe} (s) \]

**Experimental apparatus**

![Experimental apparatus diagram]

Sample mixture: Mixture of FeCl₂, Ta

Deposited sample

Quartz tube

Carbon tube

Condenser

Heat insulator

Carbon crucible

Heater

Fig. Experimental apparatus for chlorination using FeCl₂ as a chlorine source.

**Experimental condition**

\[ T = 900 \text{ K}, \ t' = 3 \text{ h}, \ \text{Ar atmosphere}, \ 
\text{Ta: 2 g, FeCl}_2 : 10 \text{ g} \]
Results

\[ 2 \text{Ta (s)} + 5 \text{FeCl}_2 (s) = 2 \text{TaCl}_5 (g) + 5 \text{Fe (s)} \]

**XRD analysis**

Residue after chlorination.
→ Fe generated at heating zone.

![XRD pattern of the residue at the heating zone.](image)

Deposit after chlorination
→ TaCl\(_5\) successfully obtained.

![XRD pattern of the deposit at the cooling zone.](image)

**ICP-AES analysis**

Fe in TaCl\(_5\) : about 20~50 ppm
Conclusions

1. Ta$_2$O$_5$ powder was obtained from capacitor scrap by the oxidation of the Ta capacitor in air, followed by mechanical and chemical treatment.

2. Ta with 99% purity was produced by a magnesiothermic reduction of the obtained Ta$_2$O$_5$ powder. Si was the major impurity.

3. The chlorination reaction of Ta and Ta$_2$O$_5$ by FeCl$_x$ was investigated, and iron free TaCl$_5$ was successfully obtained.

\[
\text{Ta (s)} + \text{FeCl}_x (s,g) = \text{TaCl}_5 (g) + \text{Fe (s)}
\]
Future works

1. The development of an effective recovery process of high-purity Ta from Ta capacitor scraps.

2. The application of chlorination reactions to some other metal scraps using chloride wastes. Chlorine recovery from chloride waste by Ti scrap is currently under investigation.