RECYCLING PROCESS FOR TANTALUM AND SOME OTHER METAL SCRAPS

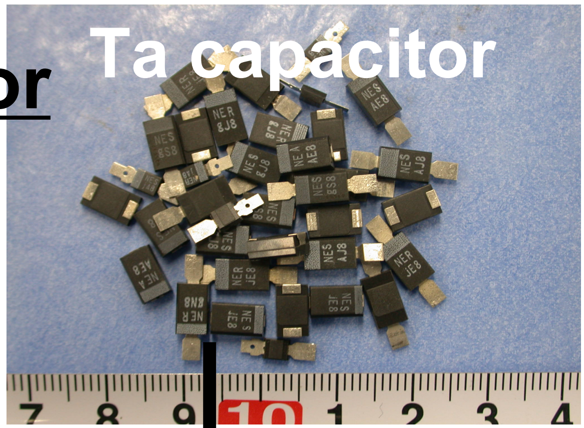
Ryosuke Matsuoka[1], Kunio Mineta[1], Toru H. Okabe[2]

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

[2]Institute of Industrial Science,
University of Tokyo, Tokyo, Japan

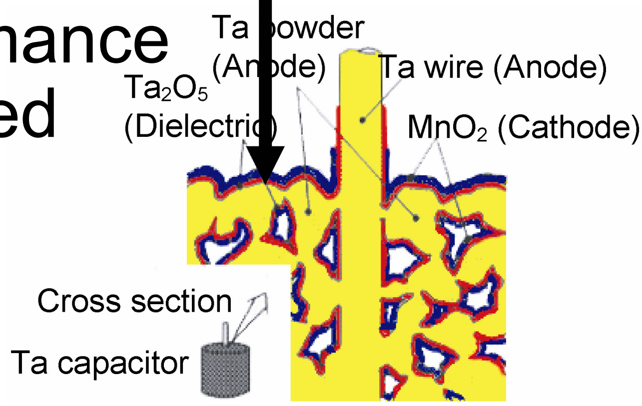
Introduction

Features of Ta capacitor



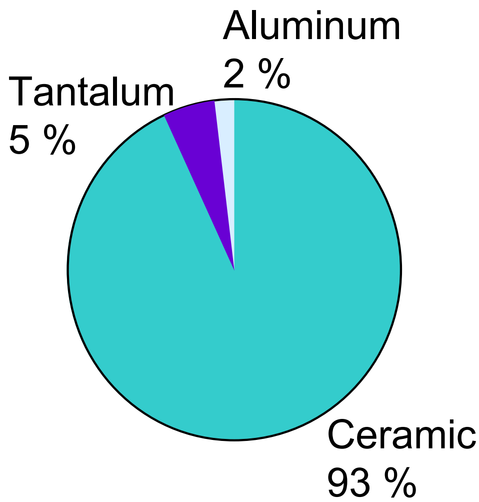
1. Largest capacity per unit volume among capacitors.
2. High thermal stability

Cross section

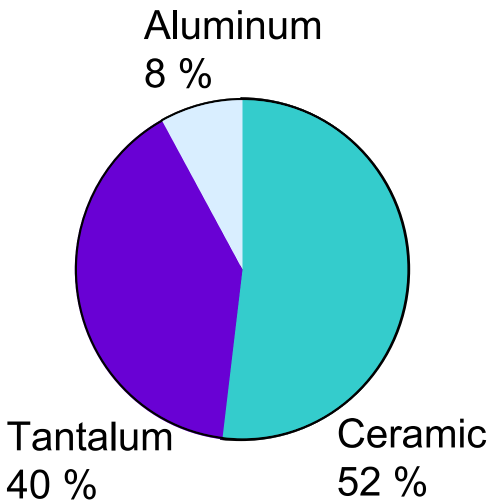


Demand for
small sized high-performance
electric devices increased
in the last 10 years

Demand for Ta capacitor is accelerated.



Unit volume



$$

Fig. The market share of capacitors in a certain computer market*1.

*1) Michael Lauri:
"Capacitor Trends in the Computer Industry", Proceedings of TIC Meeting 2000, Monday Oct. 23rd 2000 San Francisco, US.

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

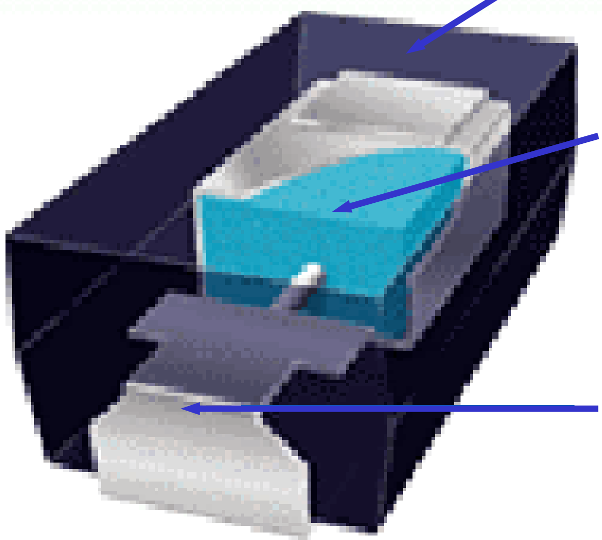
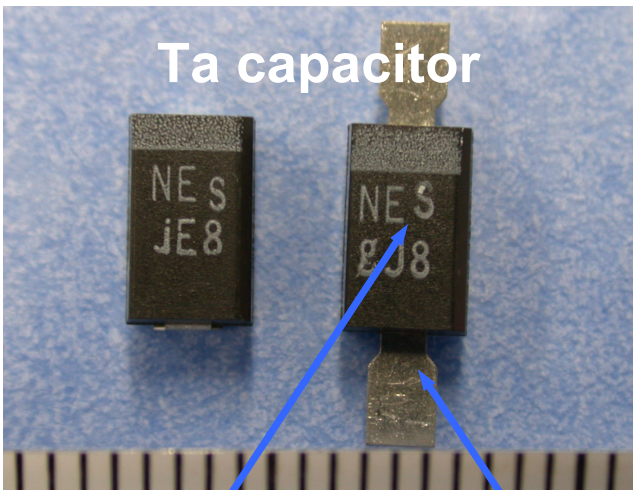


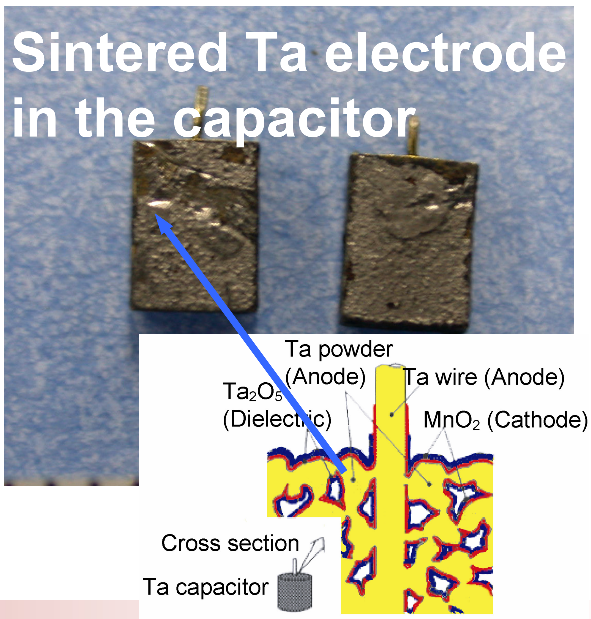
Fig. Schematic illustration of tantalum capacitor.

Ta exists in the sintered Ta electrode

Separation of sintered electrode out of the scrap is important issue



Removing external epoxy resin



Ta recovery process

Investigated Mineta and Okabe. *1

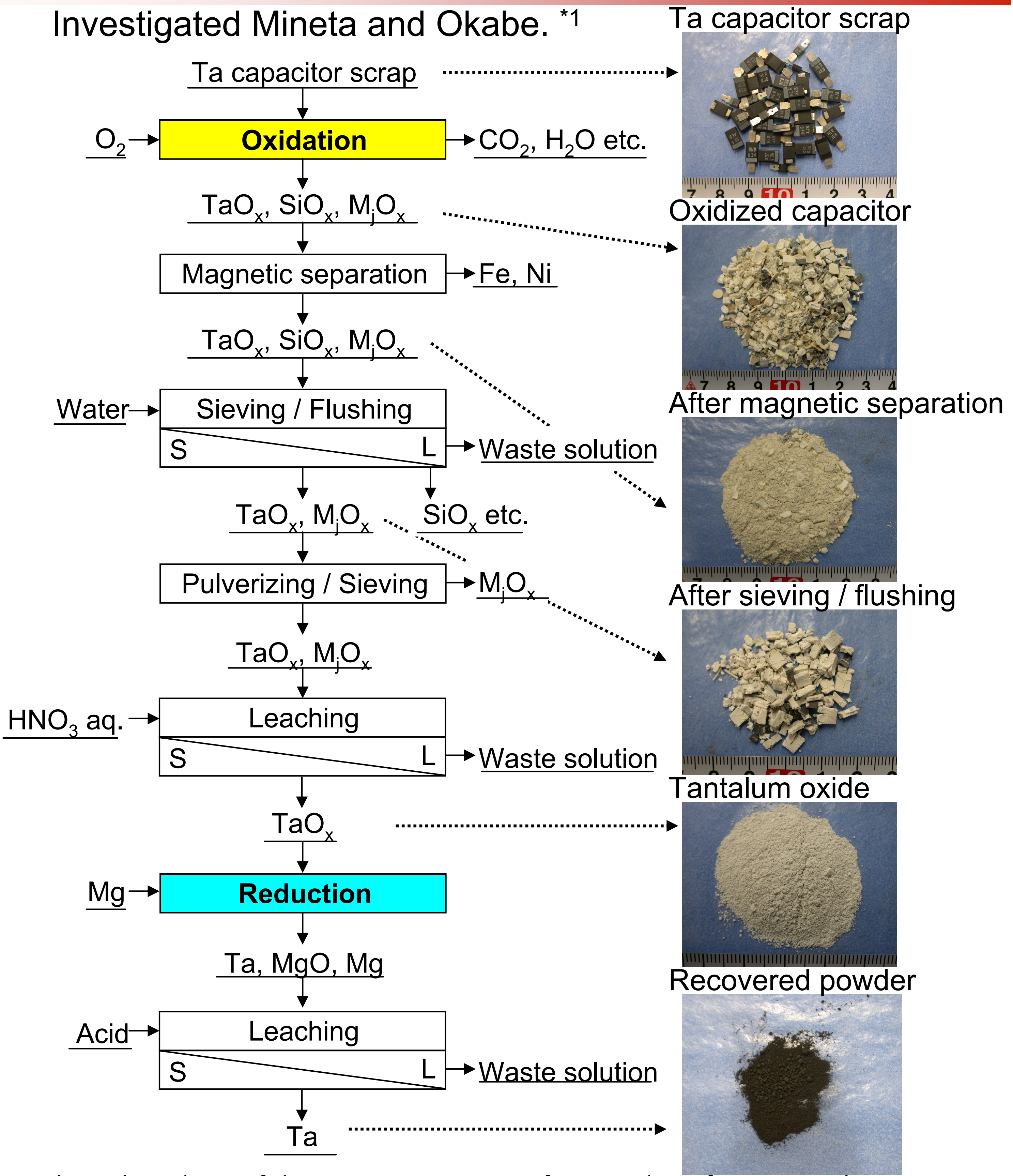


Fig. Flowchart of the recovery process for tantalum from capacitor scraps.

*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

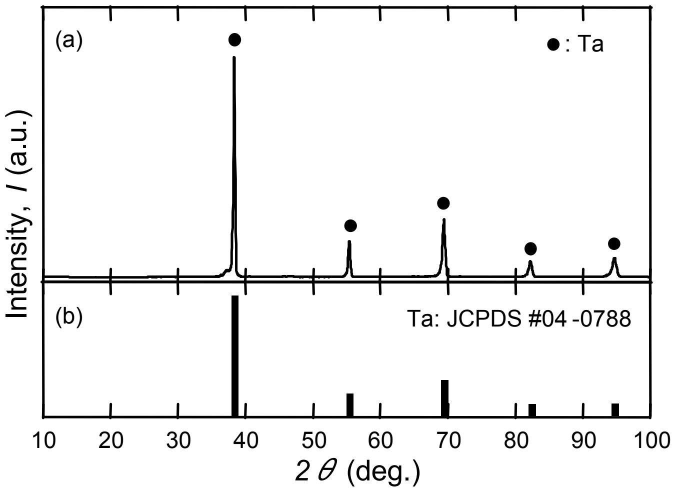


Fig. (a) XRD pattern of tantalum recovered from capacitor scraps, and (b) reference pattern of tantalum reported by JCPDS.

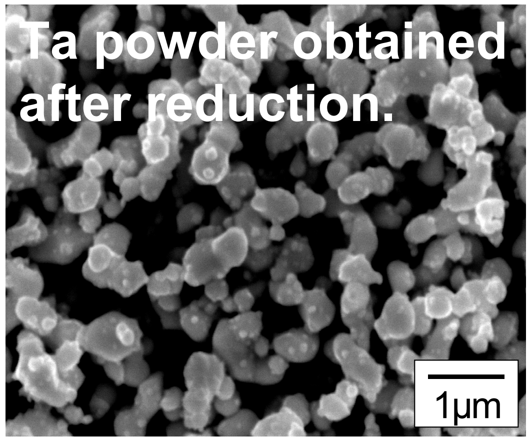


Fig. SEM image of Ta recovered from capacitor scraps.

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

	Concentration of element i, C_i (mass %)					
	Ta	Si	Cu	Ag	Fe	Mn
Capacitor scrap	(40 ~ 50)	(10 ~ 20)	(~ 5)	(-)	(5 ~ 10)	(-)
Recovered TaO_x	(80)	(-)	(-)	(-)	(-)	(-)
Obtained Ta powder	**98.57**[*1]	**0.93**	0.07	0.16	0.25	0.02

[*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

TiO_2 (+ FeO_x) + C + 2 Cl_2 → $TiCl_4$ (+ $FeCl_x$) +CO_2

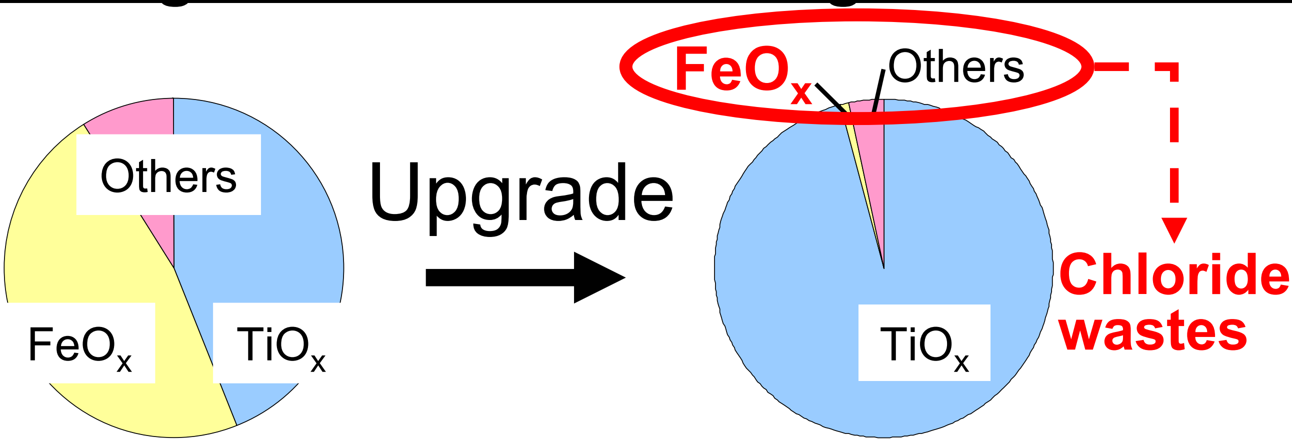
Reduction···Reduction of $TiCl_4$ using Mg

$TiCl_4$ + 2 Mg → Ti + 2 $MgCl_2$

Electrolysis ···Electrolysis of $MgCl_2$

$MgCl_2$ → Mg + Cl_2

Upgrading Ti ore for minimizing chloride wastes



Ti ore (eg. Ilmenite)

Up-graded Ilmenite (UGI)

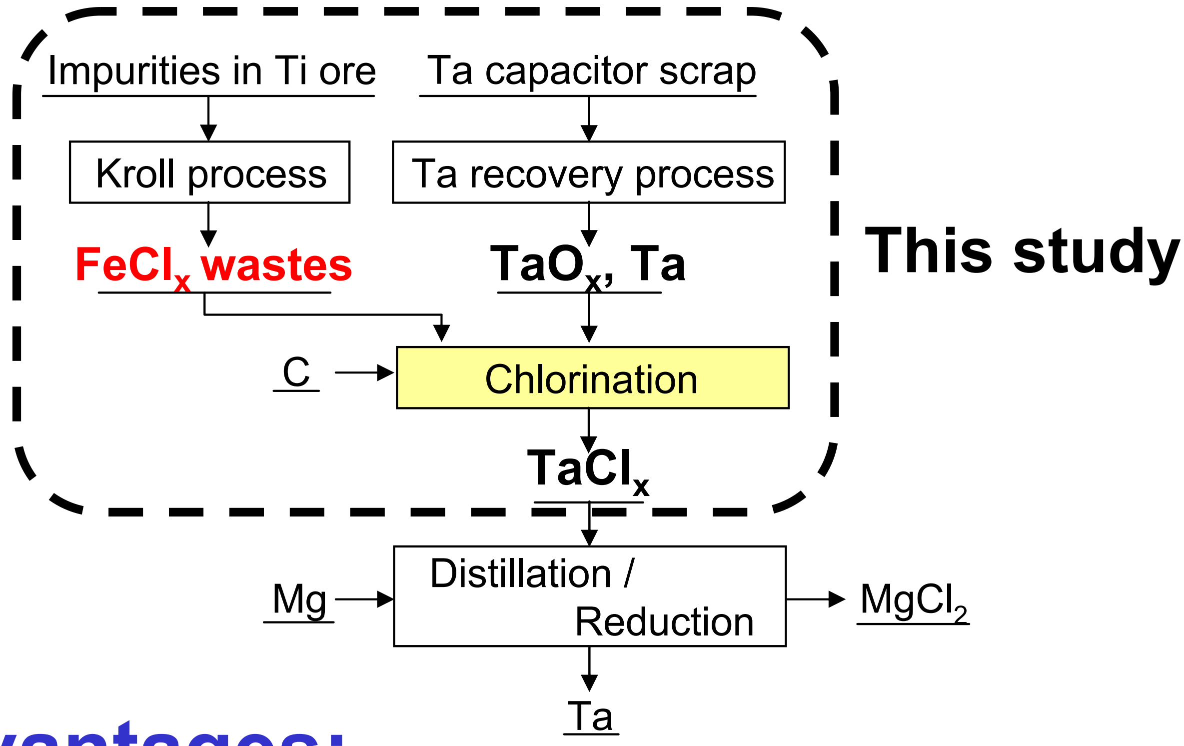
Large amount of chloride wastes (eg. $FeCl_x$) are produced in the Kroll process.

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 $FeCl_x$

$$Ta + FeCl_x \rightarrow TaCl_x + Fe$$
$$Ta_2O_5 + FeCl_x + C \rightarrow TaCl_x + Fe + CO$$



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)

Ta-Cl-O system, p_{Cl_2} = 0.1 atm

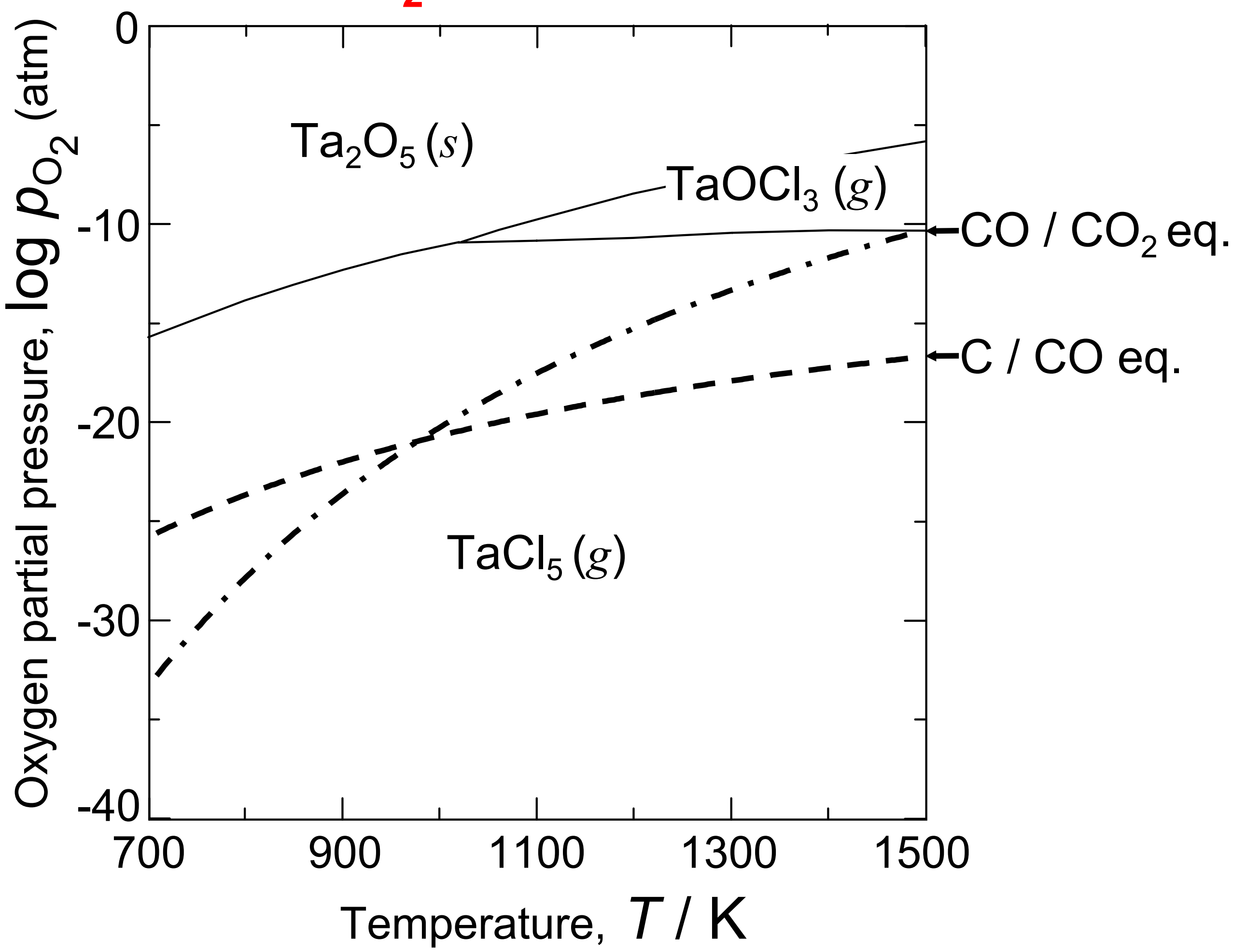


Fig. Chemical potential diagram for Ta-Cl-O system under constant chlorine partial pressure.

When C or CO is introduced in the system, chlorination of Ta_2O_5 proceeds and $TaCl_5$ (*g*) generates under high Cl_2 partial pressure.

Thermodynamic analysis (vapor pressure)

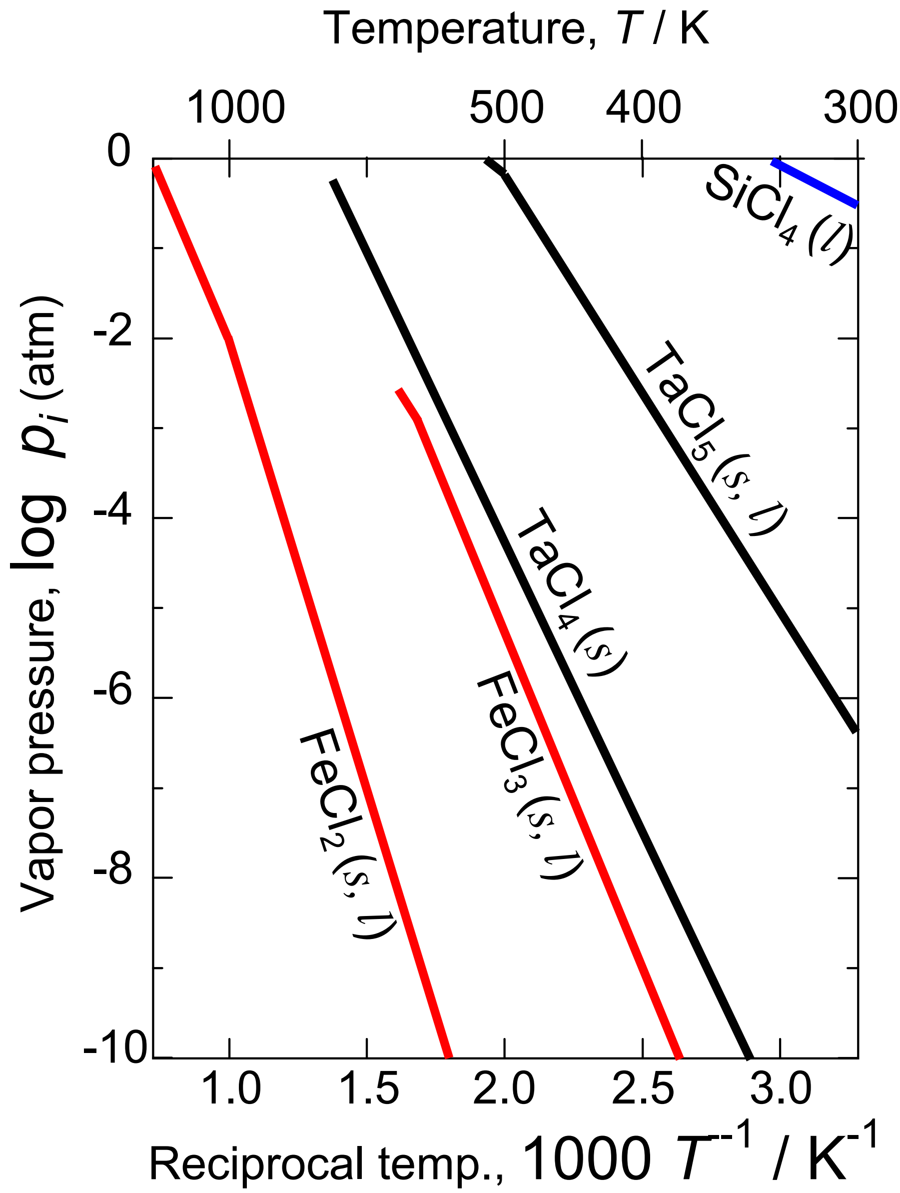


Fig. Vapor pressure of the chlorides of iron, tantalum, and silicon as a function of reciprocal temperature.

The separation of chlorides and the recovery of high-purity $TaCl_5$ (g) is possible by controlling deposition temperature.

Thermodynamic analysis (Ta chlorination)

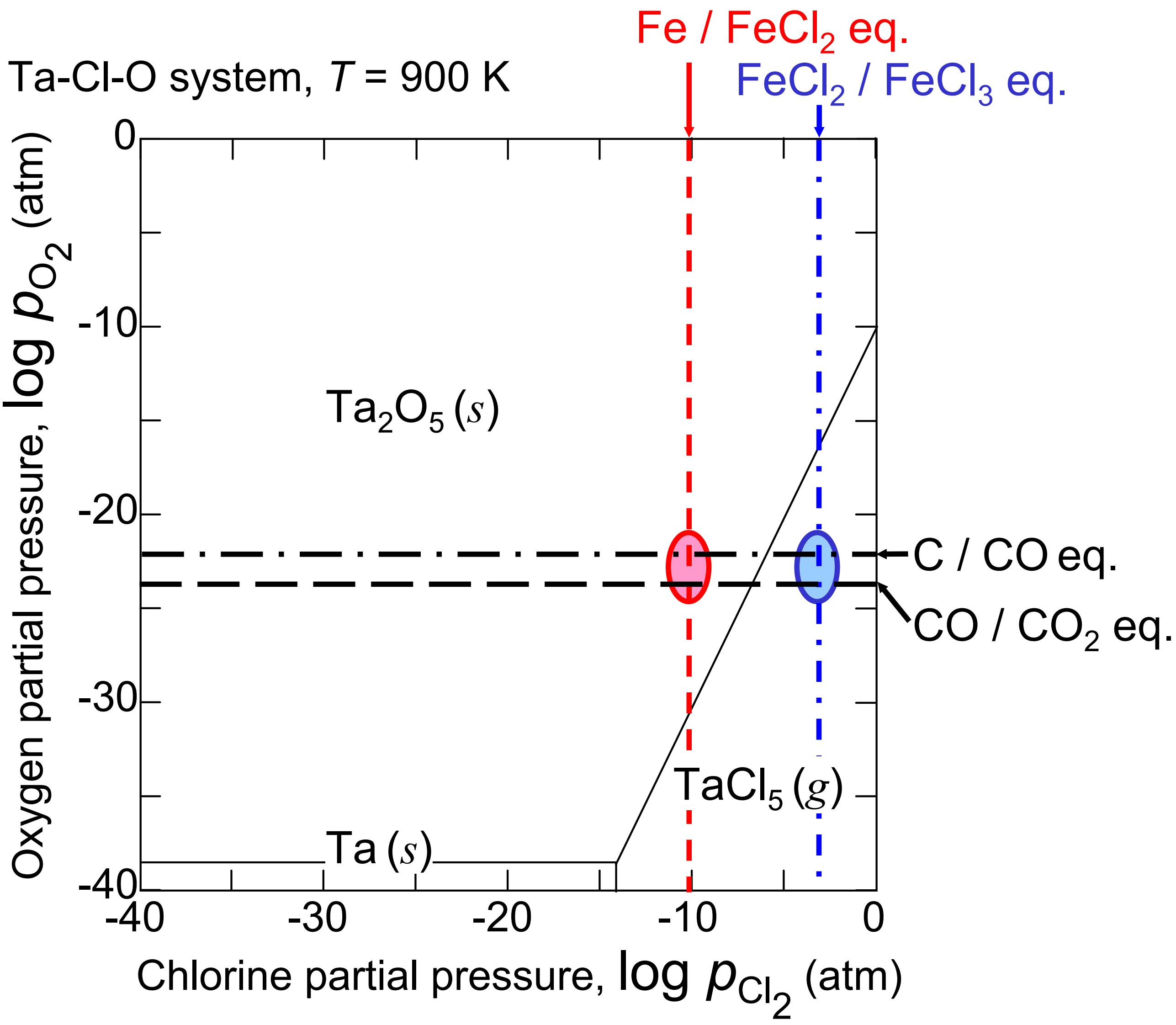


Fig. Isothermal chemical potential diagram for Ta-Cl-O system at 900 K.

Chlorination of Ta_2O_5 proceeds, when C or CO is introduced in the system.

Although Ta_2O_5 is stable under Fe / $FeCl_2$ equilibrium, chlorination of Ta_2O_5 may proceed by reducing total pressure, because vapor pressure of $TaCl_5$ is high.

Chlorination of Ta

2 Ta (*s*) + 5 $FeCl_2$ (*s,g*) = 2 $TaCl_5$ (*g*) + 5 Fe (*s*)
(or Fe_2Ta (*s*))

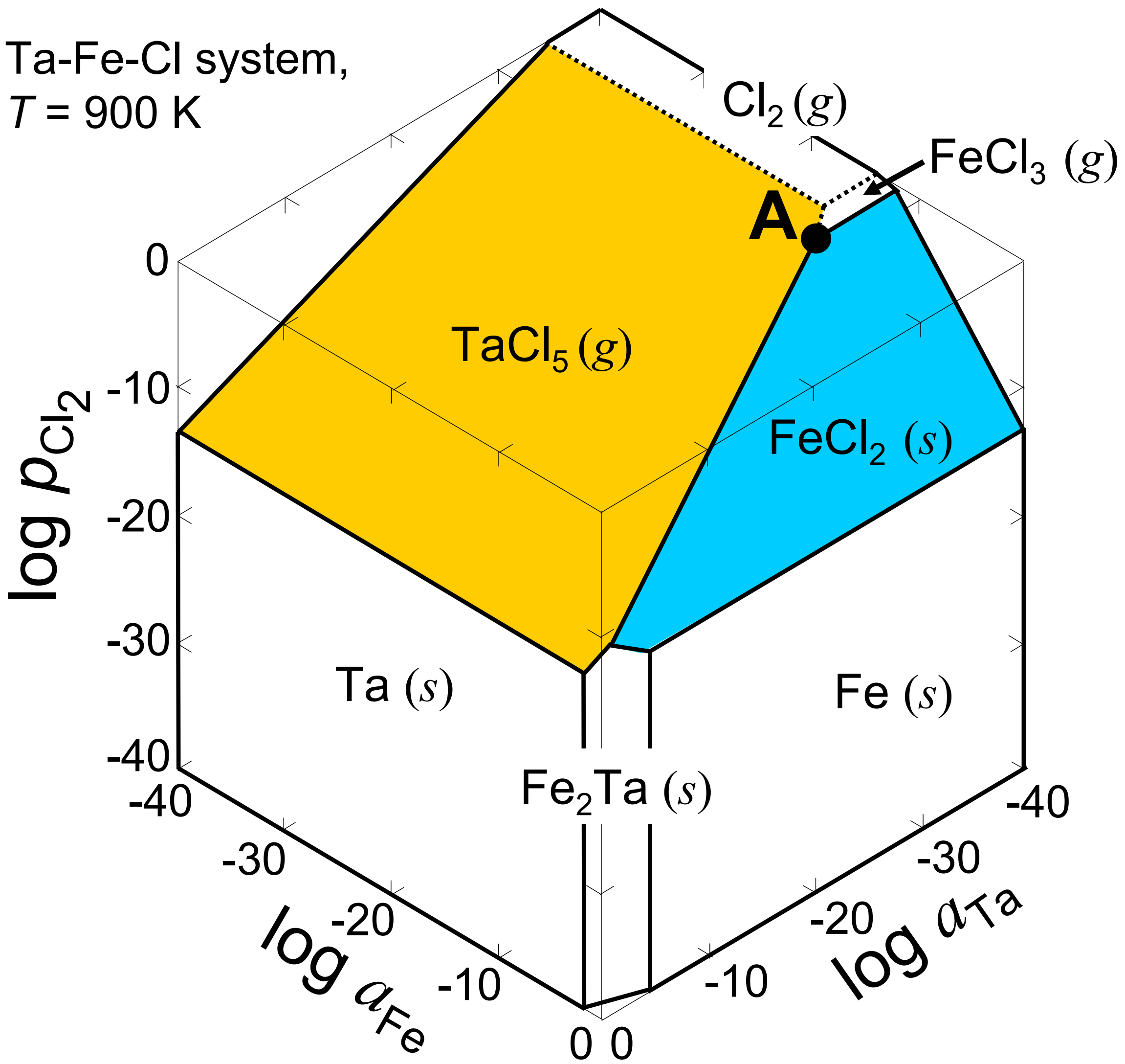


Fig. Three-dimensional chemical potential diagram of Ta-Fe-Cl system at 900 K.

$TaCl_5$ can be generated by reacting Ta and $FeCl_2$ or $FeCl_3$.

Chlorination of Ta using $FeCl_2$

$$2\ \mathrm{Ta}\ (s) + 5\ \mathrm{FeCl_2}\ (s) = 2\ \mathrm{TaCl_5}\ (g) + 5\ \mathrm{Fe}\ (s)$$

Experimental apparatus

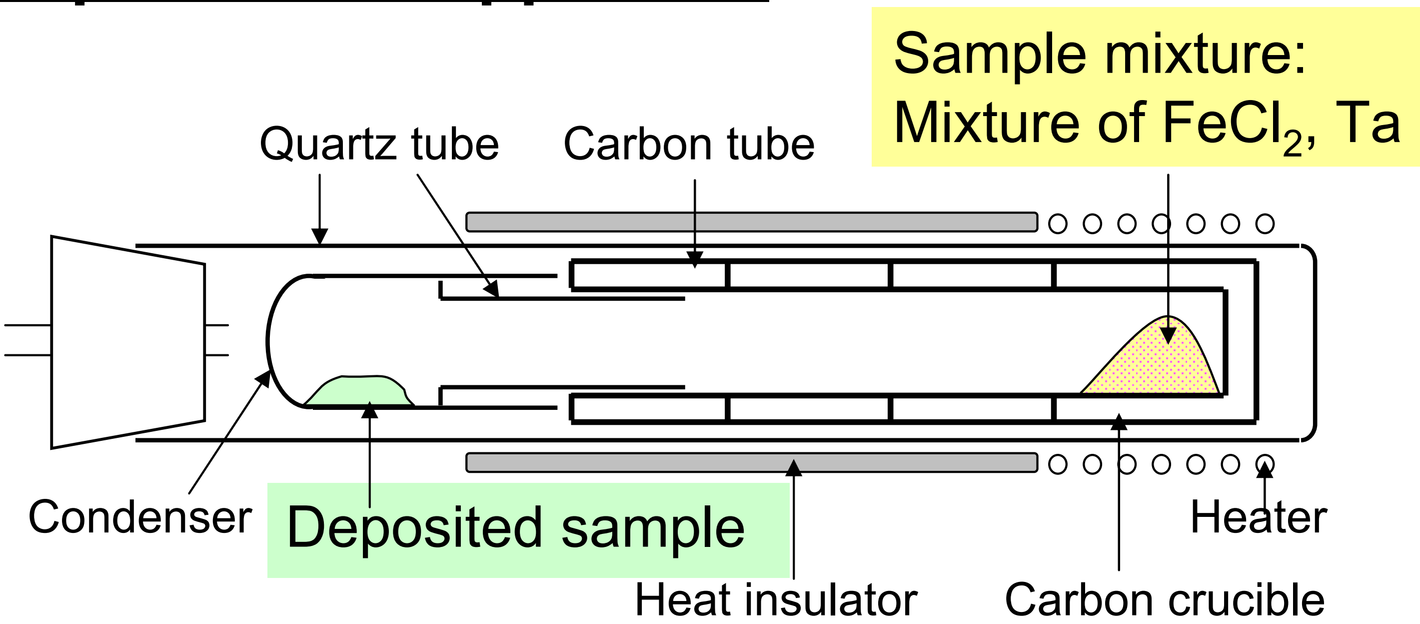


Fig. Experimental apparatus for chlorination using $FeCl_2$ as a chlorine source.

Experimental condition

***T* = 900 K, *t'* = 3 h, Ar atmosphere,**
Ta: 2 g, $FeCl_2$: 10 g

Results

$2\ Ta\ (s) + 5\ FeCl_2\ (s) = 2\ TaCl_5\ (g) + 5\ Fe\ (s)$

XRD analysis

Residue after chlorination.
→ Fe generated at heating zone.

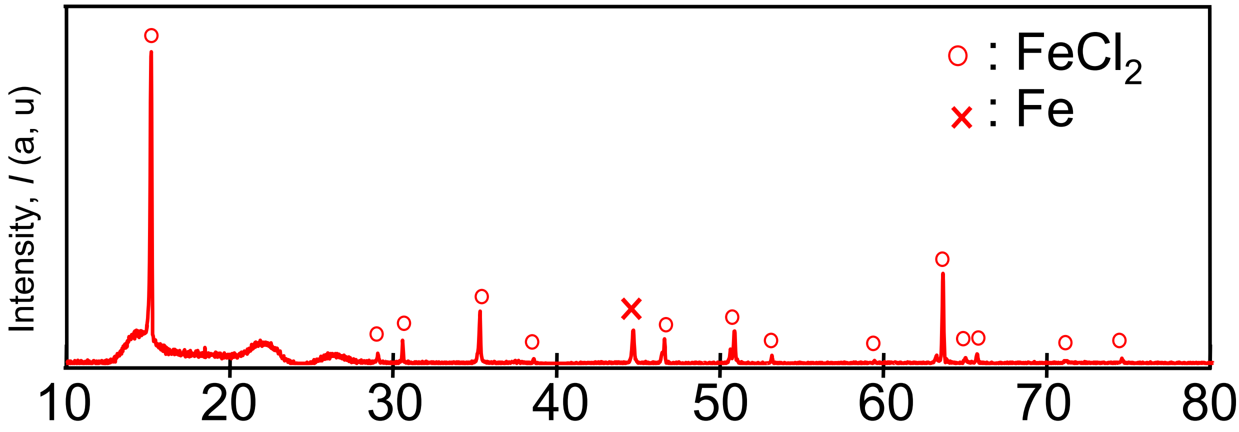


Fig. XRD pattern of the residue at the heating zone.

Deposit after chlorination
→$TaCl_5$ successfully obtained.

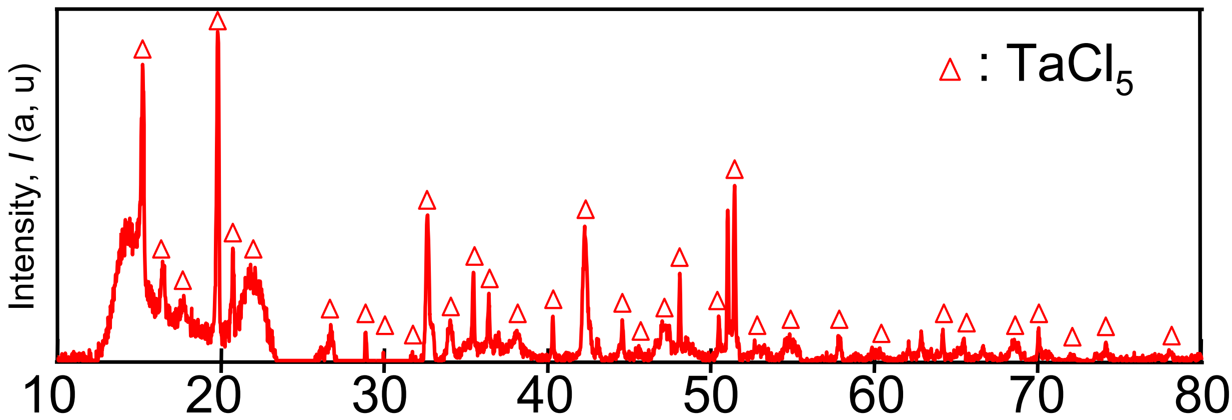


Fig. XRD pattern of the deposit at the cooling zone.

ICP-AES analysis

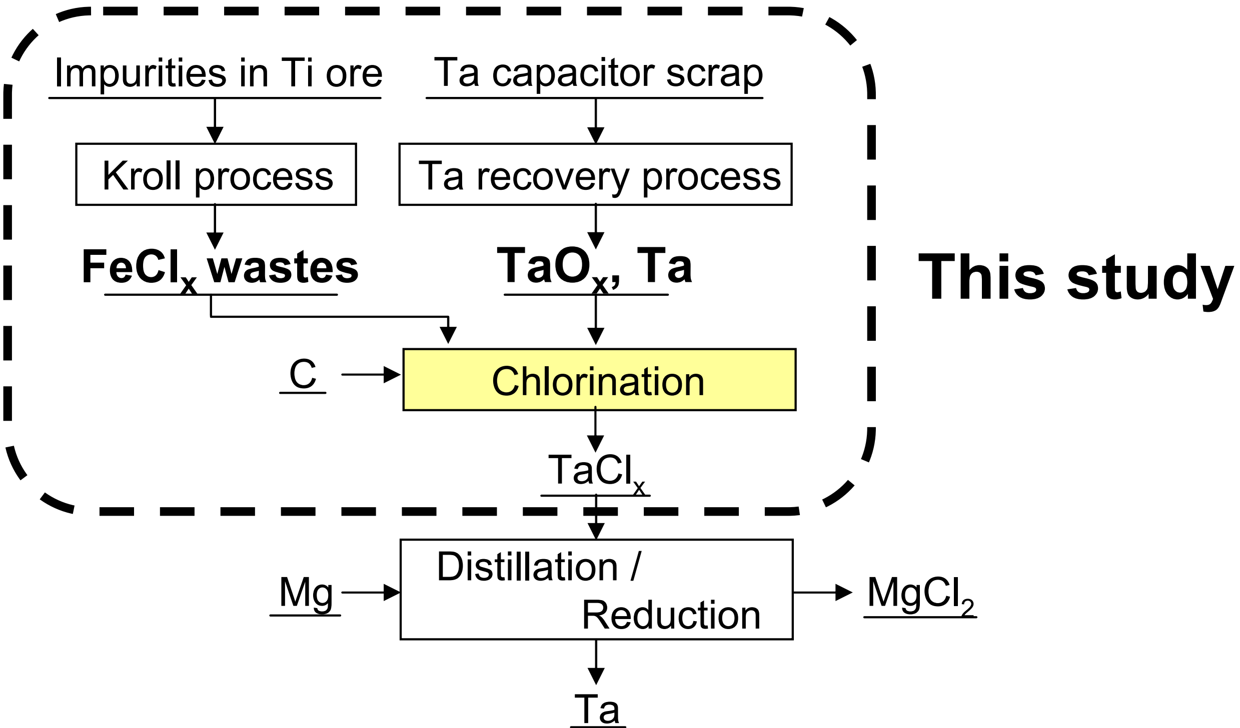
Fe in $TaCl_5$: about 20~50 ppm

Conclusions

1. Ta_2O_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_2O_5 powder.
   Si was the major impurity.

3. The chlorination reaction of Ta and Ta_2O_5 by $FeCl_x$ was investigated, and iron free $TaCl_5$ was successfully obtained.



$$Ta\ (s) + FeCl_x\ (s,g) = TaCl_5\ (g) + Fe\ (s)$$

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.