

RECYCLING PROCESS FOR TANTALUM AND SOME OTHER METAL SCRAPS

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Abstract

A recycling process for tantalum from capacitor scraps using an oxidation process followed by mechanical separation and chemical treatment was investigated. This study demonstrates that sintered tantalum electrodes inside the capacitor scraps can be mechanically collected after the oxidation of the scraps in air, and high-purity tantalum oxide powder (Ta_2O_5) was efficiently recovered after chemical treatment. By reducing the Ta_2O_5 obtained through magnesiothermic reduction, tantalum powder with 99 mass% purity was obtained. Using the chlorination for tantalum recovery was also investigated, and the tantalum or tantalum compounds were reacted with chloride wastes such as FeCl_x . It was found that tantalum was effectively separated and purified when tantalum powder is reacted with FeCl_x at 1100 K under an argon atmosphere. This recycling process utilizing chloride scrap has now been extended to other reactive metals such as titanium.

Introduction

In recent times, the demand for tantalum capacitors has been increasing owing to the wide spread use of cellular phones, notebook computers, and small electric appliances. This is because, these are high-performance capacitors that have a large capacity and high thermal stability compared to other capacitors. Currently, the world annual production of tantalum is about 2000 tons, and most of the tantalum metal produced is used for tantalum capacitors. The price of tantalum powder fluctuates sharply as the production volume of tantalum is limited. For instance, in the year 2000, the demand for tantalum increased, and the price of tantalum ore increased to six times that in 1999. As a result, capacitor manufacturers encountered a material crisis in the supply of tantalum. In recent years, the tantalum market has been fairly stable, but the price of high-purity tantalum powder for capacitors is several hundred dollars per kilogram, which is still expensive. Although a large amount of off-spec tantalum capacitors are generated during the manufacturing process, an efficient recycling process has not been established to recover them. Most of the tantalum scrap obtained from capacitors is exported overseas and treated with tantalum ore, which contains a large amount of niobium. Tantalum and niobium are related elements, having similar chemical characteristics, and a large amount of energy is required to isolate tantalum from the ore containing niobium. Furthermore, a large amount of waste solution is generated during the purification process. On the other hand, tantalum present in the capacitor scrap does not contain any niobium, and it can be considered a high-quality ore. It is, therefore, important to establish a new recycling process to recover tantalum from capacitor scrap or other tantalum scraps.

Recycling Process of a Tantalum Capacitor

Figure 1 is a schematic illustration of a tantalum capacitor. As shown in Fig. 1 (a), the tantalum capacitor is roughly divided into three components: a terminal, a packing of fireproof epoxy resin, and a sintered tantalum electrode. The terminal is made of iron, nickel, or copper. The fireproof epoxy resin is a polymer, in which silicon oxide (SiO_2) powder is added to enhance its thermal stability. The sintered tantalum electrode, which is schematically shown in Fig. 1 (b), is made of fine tantalum powder and other trace elements, and it contains 90 mass% or a higher content of tantalum. It is rational to recover the sintered tantalum electrode from the capacitor before chemical treatment, because tantalum exists in the sintered tantalum electrode only at a high concentration. Since the epoxy resin coats the tantalum electrode very tightly, the authors employed an oxidizing procedure for recovering these tantalum electrodes before mechanical and chemical treatment [1].

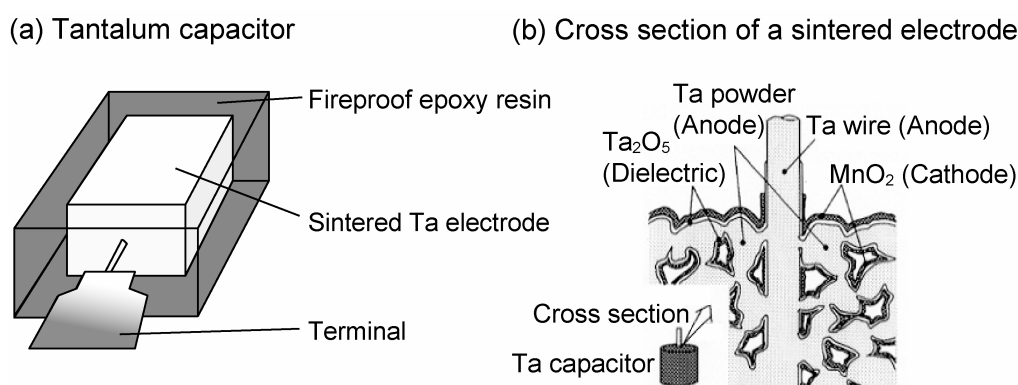


Figure 1. Configuration of a tantalum capacitor.

Figure 2 (a) shows a flowchart of the recovery process of tantalum from capacitor scraps investigated in this study. This process has two major steps. The first step involves the collection of tantalum from capacitor scraps by oxidation and mechanical separation and chemical treatment, and the second step involves the recovery of metallic tantalum by conventional metallothermic reduction followed by leaching.

To collect the sintered tantalum electrodes, tantalum capacitor scraps (Fig. 2 (b)) were heated in the air at 1150 K for 30 min, and the epoxy resin was oxidized (Fig. 2 (c)). The iron and nickel terminals were removed by magnetic separation, because these terminals were disconnected from the electrodes after oxidation (Fig. 2 (d)). After oxidation, the epoxy resin became a powder, which is chiefly consisted of SiO_2 . The sintered tantalum electrode retained its original shape even though it was oxidized, and it was easy to separate the SiO_2 powder by sieving. After sieving, the sample was washed with water to flush out the SiO_2 powder completely (Fig. 2 (e)). The sample was then pulverized, and tantalum oxide (Ta_2O_5) powder was easily obtained. On the other hand, the copper terminals did not break; they retained their original shape because they possessed metallic ductility. The copper terminals were removed by sieving. The obtained tantalum oxide, containing copper fragments and other impurities, was treated in nitric acid to remove the impurities. The powder obtained after rinsing with water was calcinated in the air at 1273 K for 1 h to remove water and carbon. Tantalum in the capacitor scraps was recovered as pure tantalum oxide powder (Fig. 2 (f)).

The tantalum oxide obtained was sealed in a stainless steel vessel and reduced by magnesium vapor at 1273 K for 6 h. After reduction, the sample containing tantalum, magnesium, and magnesium oxide (MgO) was treated in hydrochloric acid and acetic acid to remove the

magnesium and MgO. The tantalum powder obtained was then rinsed with distilled water, alcohol, and acetone, and then dried in a vacuum (Fig. 2 (g)).

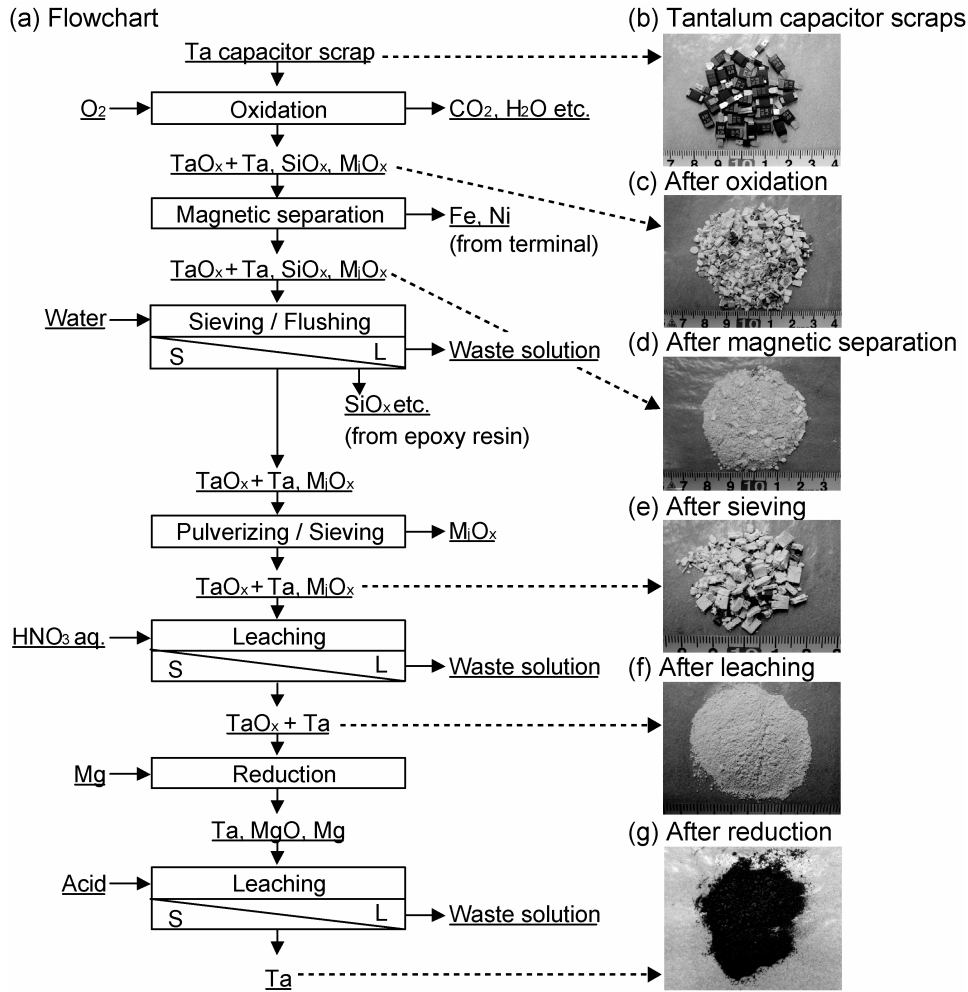


Figure 2. (a) Flowchart of the recovery process for tantalum from capacitor scraps. (b) Tantalum capacitor scrap used in the study. (c) Tantalum capacitor after oxidation (temperature: 1150 K, holding time: 30 min). (d) After magnetic separation. (e) After removal of SiO_2 powder by sieving. (f) Ta_2O_5 powder obtained after leaching. (g) Ta powder obtained after reduction.

Table I shows a representative result of a chemical analysis of the tantalum powder obtained, which was determined by an inductivity coupled plasma-atomic emission spectroscopy (ICP-AES). The purity of the obtained tantalum was approximately 99 mass% and a major impurity was silicon, which can be attributed to the SiO_2 present in the epoxy resin. It was difficult to completely remove SiO_2 from this sample by the process shown in Fig. 2, because the silicon separation in this process is based on mechanical separation (sieving and flushing). Additional purification processes may be required to obtain higher quality tantalum. For this reason, the authors are currently investigating a purification process for recovering tantalum from scrap [2].

Table I. Analytical result of tantalum powder determined by ICP-AES analysis.
The data in parenthesis are estimated value.

	Concentration of element i , C_i (mass%)					
	Ta	Si	Cu	Ag	Fe	Mn
Tantalum capacitor	(40 ~ 50)	(10 ~ 20)	(~ 5)	(-)	(5 ~ 10)	(-)
Ta powder obtained after reduction	98.57*1	0.93	0.07	0.16	0.25	0.02

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

Thermodynamic Discussion on Chlorination of Tantalum

In this section, a new chlorination process for tantalum and other metal scraps, utilizing chloride waste generated from the titanium production process, is investigated. Currently, titanium is produced commercially by the Kroll process [3,4], and this process involves three major steps. The first step involves the chlorination of titanium ore by chlorine gas under a carbon-saturated atmosphere, followed by purification of titanium chloride (TiCl_4) produced during this process. The second step involves the reduction of TiCl_4 using a magnesium reductant, in which sponge titanium and magnesium chloride (MgCl_2) are produced. In the third step, the MgCl_2 is recovered and converted into magnesium and chlorine by molten salt electrolysis, and the products are returned to the chlorination and reduction process. Efficient circulation of magnesium and chlorine is a feature of the Kroll process. However, a considerable amount of chloride wastes, such as FeCl_x , are generated from the chlorination process, because titanium ore contains impurities such as iron. Chloride waste disposal is a laborious and expensive process. Furthermore, additional chlorine gas has to be purchased to compensate for the chlorine loss caused by the generation of chloride wastes. The generation of chloride wastes also leads to environmental issues, because there is no effective method to recycle them. For this reason, upgraded ilmenite (UGI), which contains titanium oxide with approximately 95 % purity, is currently used as a raw material in the Kroll process in order to minimize the generation of chloride wastes [5].

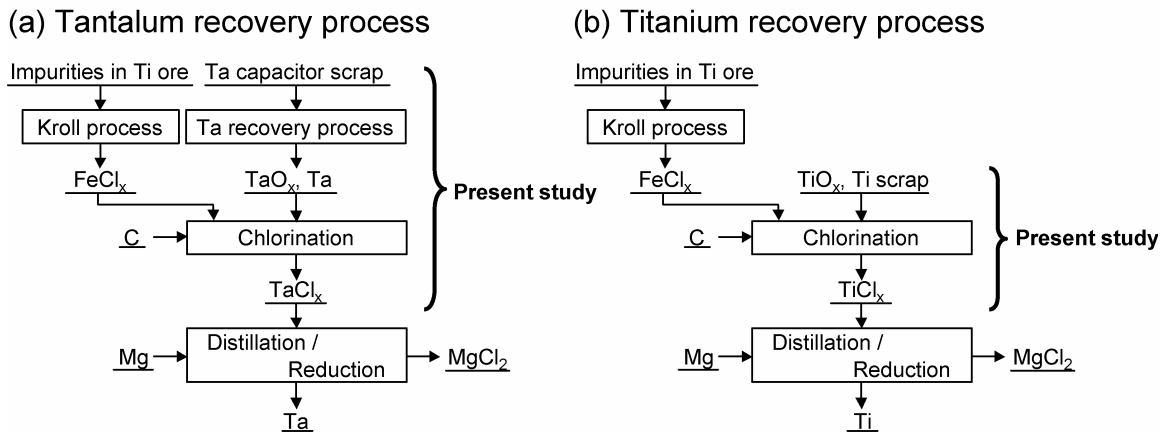


Figure 3. Scrap recovery process of tantalum and titanium.

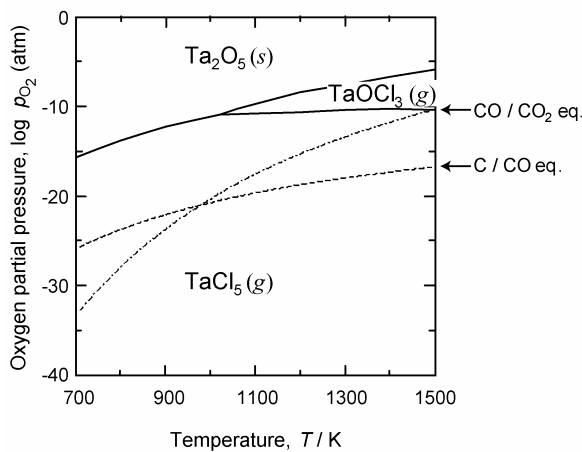
In this study, the feasibility of a new chlorination process is analyzed from a thermodynamic viewpoint. In the process shown in Figure 3 (a), tantalum and Ta_2O_5 , which are recovered from tantalum capacitors, are chlorinated by utilizing the chlorine from the chloride wastes generated in the Kroll process and higher quality tantalum can be obtained. In this process, tantalum is purified by a chlorination reaction, and at the same time, chlorine in the wastes is also recovered. If chlorine in the chloride wastes generated from titanium smelting can be recovered

effectively and utilized in the chlorination procedure, the problem of chloride waste disposal can be minimized and the loss of chlorine in the Kroll process can be decreased. In addition, low-grade titanium ore, which is much cheaper than UGI, can be used in the Kroll process, if an effective recovery process for chlorine is established. With this background, a thermodynamic analysis of the reactions between FeCl_x and tantalum or tantalum oxides was carried out in this study.

Figure 4 (a) shows a chemical potential diagram for the Ta-Cl-O system under a constant chlorine partial pressure ($p_{\text{Cl}_2} = 0.1$ atm). The diagram is constructed on the basis of the thermodynamic values [6]. Thermodynamically stable phases are shown in this figure as a function of oxygen partial pressure, p_{O_2} , and temperature, T . The dashed and chain lines plotted in the figure represent equilibrium oxygen partial pressure under C / CO and CO / CO_2 equilibrium, respectively. This figure shows that chlorination of Ta_2O_5 proceeds, and TaCl_5 is generated when carbon or CO is introduced into the system under a high p_{Cl_2} atmosphere. When p_{O_2} is high, Ta_2O_5 and TaOCl_3 are stable, and TaCl_5 cannot be obtained even under a high p_{Cl_2} atmosphere.

Figure 4 (b) shows the isothermal chemical potential diagram for the Ta-Cl-O system at 1100 K, plotted with chlorine partial pressure, p_{Cl_2} , as abscissa and oxygen partial pressure, p_{O_2} , as ordinate. In the figure, equilibrium oxygen partial pressure under C / CO and CO / CO_2 equilibrium, and equilibrium chlorine partial pressure under FeCl_2 / FeCl_3 and Fe / FeCl_2 equilibrium are depicted as dashed and chain lines, respectively. The intersections of these lines are labeled as points A, B, C, and D. The figure shows that TaCl_5 is stable at points A and B ($p_{\text{Cl}_2} = 0.1$ atm) [6], and the chlorination of Ta_2O_5 proceeds when FeCl_3 is reacted with Ta_2O_5 in the presence of carbon or CO. Ta_2O_5 is stable at points C and D ($\text{Fe} / \text{FeCl}_2$ eq., $p_{\text{Cl}_2} = 8.0 \times 10^{-11}$ atm), and the chlorination of Ta_2O_5 by FeCl_2 is difficult even at a low p_{O_2} . When the total pressure of the system is decreased, TaCl_5 gas may be generated even at points C and D, since the vapor pressure of TaCl_5 is high.

(a) Under constant chlorine partial pressure ($p_{\text{Cl}_2} = 0.1$ atm)



(b) Isothermal predominance diagram at 1100 K

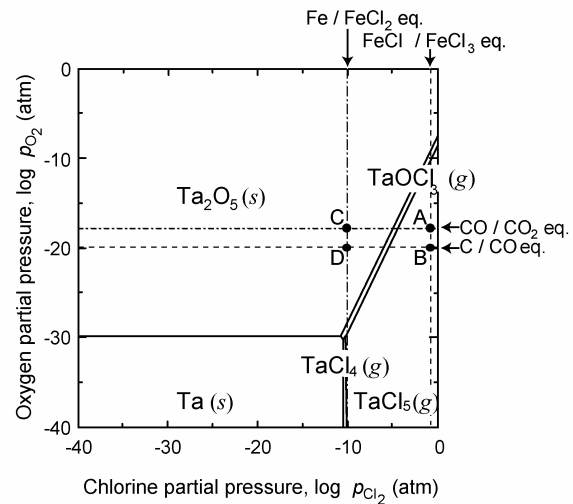
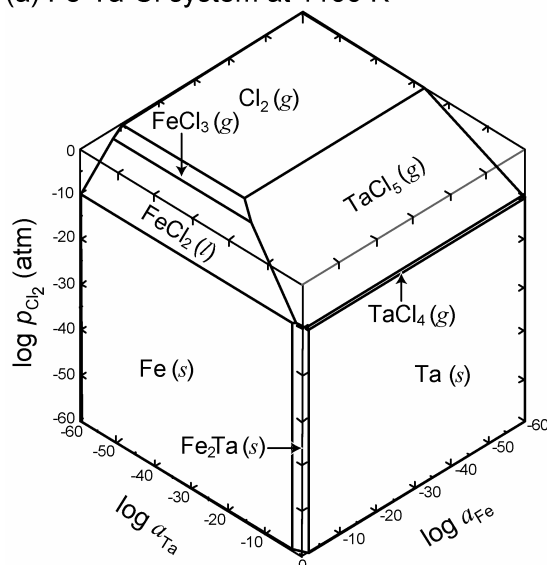


Figure 4. Chemical potential diagrams for the Ta-Cl-O system.

Figure 5 (a) shows a 3-D chemical potential diagram for the Fe-Ta-Cl system at 1100 K. The most stable phases are shown as a plane in the 3-D space. The figure shows that TaCl_5 can be generated by reacting FeCl_2 and tantalum, when tantalum activity (a_{Ta}) is high. Under certain

conditions, an intermetallic compound, Fe_2Ta , may be formed during the chlorination reaction of tantalum; however, all the tantalum is expected to be chlorinated by adding a large amount of FeCl_x into the oxygen-free system.

(a) Fe-Ta-Cl system at 1100 K



(b) Fe-Ti-Cl system at 1100 K

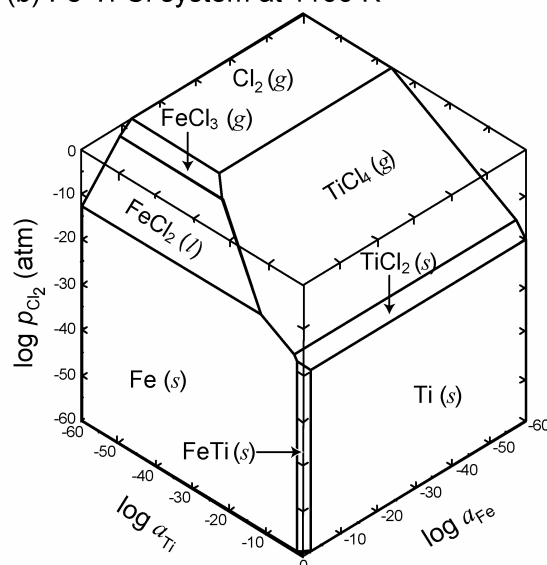


Figure 5. Chemical potential diagrams for the Fe-Ta-Cl and Fe-Ti-Cl systems.

Tantalum chloride produced by the chlorination reaction can be transferred in the gas phase and recovered by condensing chloride at lower temperatures. Figure 6 shows the vapor pressure of chlorides as a function of reciprocal temperature. The vapor pressure of TaCl_5 is very different from that of SiCl_4 (b.p. = 330 K) [6], which is the chloride of the main impurity (SiO_2) in the tantalum obtained from capacitor scraps. The vapor pressure of TaCl_5 is also different from that of FeCl_x , which always coexists in the chlorination reaction.

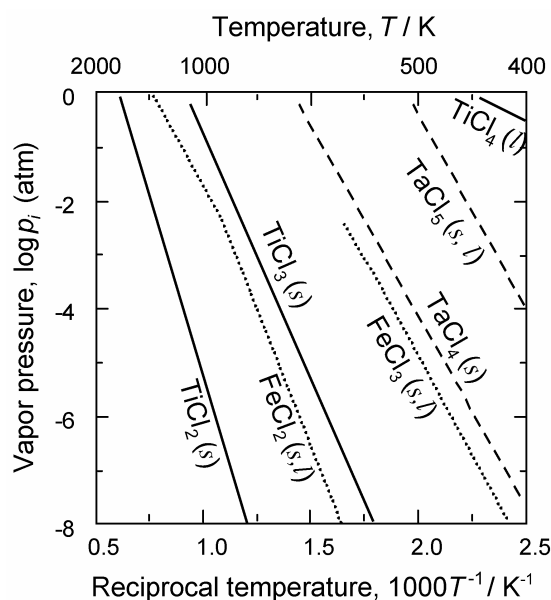


Figure 6. Vapor pressure of chlorides as a function of reciprocal temperature.

Based on the thermodynamic analysis mentioned above, the authors are currently conducting experimental work for obtaining tantalum chloride by reacting tantalum and FeCl_x . In the preliminary experiment, TaCl_5 was successfully obtained by controlling the deposition

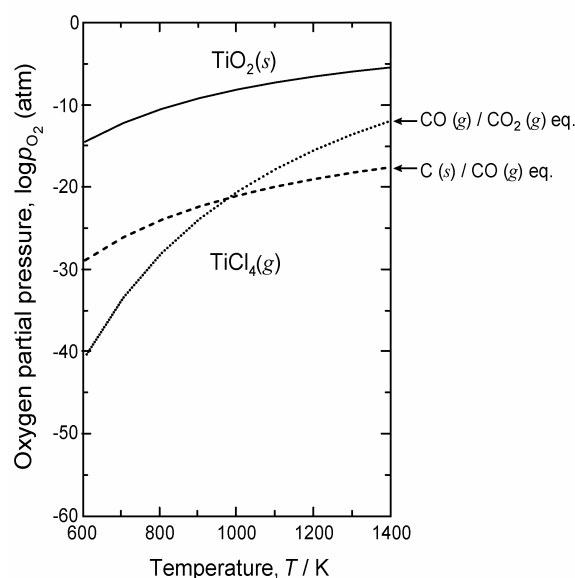
temperature after reacting 2 g of tantalum and 6 g of FeCl_2 at 900 K, in the carbon crucible, under an argon atmosphere.

Thermodynamic Discussion on Chlorination of Titanium

In this section, the chlorination of titanium is discussed using chemical potential diagrams. The purpose of this study is to develop a new chlorination process that utilizes the chlorine present in the chloride wastes generated from titanium smelting. Since the production volume of titanium is considerably larger than that of tantalum, the chlorine recovery process from the chloride waste may be highly efficient if titanium scrap can be utilized. For this reason, the chlorination between FeCl_x and titanium or TiO_2 , has been considered from the thermodynamic viewpoint.

Figure 3 (b) shows a flowchart of the titanium chlorination process using the iron chloride wastes generated in the Kroll process. Figure 5 (b) shows a 3-D chemical potential diagram for the Fe-Ti-Cl system at 1100 K. The figure shows that equilibrium chlorine partial pressure under Fe / FeCl_2 equilibrium lies in the stable region of TiCl_4 gas. The vapor pressure of titanium chlorides, as a function of reciprocal temperature, is plotted in Fig. 6. Figures 7 (a) and (b) show the chemical potential diagrams for the Ti-Cl-O system under constant chlorine partial pressure at 0.1 atm and that for an isothermal predominance diagram at 1100 K, respectively. These diagrams for the titanium system shown in Fig. 3 (b), 5 (b), 6, 7 (a), and 7 (b) are similar to those for the tantalum system discussed in the previous section; however, the stability region of TiCl_4 is larger than that of TaCl_5 . Similar to the tantalum system, the chlorination of TiO_2 proceeds when FeCl_3 is reacted with TiO_2 in the presence of carbon or CO. It is difficult to chlorinate TiO_2 by FeCl_2 even in the presence of carbon or CO. However, when the total pressure of the system is decreased, TiCl_4 may be generated even under an Fe / FeCl_2 equilibrium, since the vapor pressure of TiCl_4 is high.

(a) Under constant chlorine partial pressure ($p_{\text{Cl}_2} = 0.1 \text{ atm}$)



(b) Isothermal predominance diagram at 1100 K

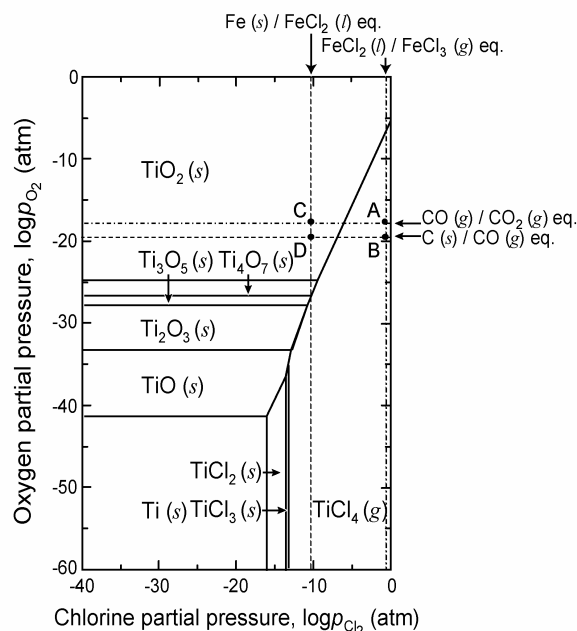


Figure 7. Chemical potential diagrams for the Ti-Cl-O system.

Although it is difficult to recover the chlorine in FeCl_2 using TiO_2 , FeCl_2 can be reacted with titanium metal, and TiCl_4 is generated in the oxygen-free system (Fig. 5 (b)). A thermodynamic analysis shows that metallic titanium can be used to extract chlorine from the FeCl_2 waste. As

the amount of titanium scrap increases in the future, the chlorine recovery process from chloride wastes may become an important process.

Conclusions

The recovery of tantalum from capacitor scraps using an oxidation process followed by mechanical and chemical treatment was investigated, and tantalum with 99 mass% purity was obtained after magnesiothermic reduction. It was difficult to remove SiO_2 by the process investigated in this study, because silicon separation is based on a mechanical separation method. To obtain higher quality tantalum, a chlorination process for further purification was discussed thermodynamically.

As seen in the results of the thermodynamic analysis, the chlorination of Ta_2O_5 proceeds when FeCl_3 is reacted with Ta_2O_5 in the presence of carbon or CO. Furthermore, the chlorination between FeCl_x and titanium or TiO_2 was considered. Chemical potential diagrams for the titanium system are similar to those for the tantalum system, and the chlorination of TiO_2 proceeds when FeCl_3 is reacted with TiO_2 in the presence of carbon or CO. Thermodynamically, it is difficult to extract the chlorine in FeCl_2 when using TiO_2 or Ta_2O_5 . However, a thermodynamic analysis revealed that metallic tantalum or titanium reacts with FeCl_2 , and the chlorine in the chloride wastes can be extracted as TaCl_5 or TiCl_4 gas.

If chlorine in the chloride wastes, generated from titanium smelting, can be recovered effectively, the problem of disposal of chloride waste will be minimized and the loss of chlorine in the process will decrease. Currently, the authors are conducting experimental work to obtain tantalum chloride or titanium chloride by reacting FeCl_x chloride wastes with tantalum or titanium scrap.

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