Chlorination-Volatilization Behavior of Titanium Metal Scraps during Recycling Using Reaction-Mediating Molten Salt

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In order to develop an efficient and environmentally friendly process for recycling both titanium scrap and FeCl_x ($x = 2, 3$) waste, the chlorination-volatilization of titanium metal scraps utilizing a MgCl_2 - SmCl_3 reaction-mediating molten salt was examined. After the thermodynamic analyses on the chlorination behavior of representative elements such as the alloying elements and oxygen, fundamental experiments were carried out at 1100 K by reacting off-grade Ti sponge, Ti-6Al-4V alloy rod, and Ti rod with MgCl_2 - SmCl_3 molten salt. The results indicated that TiCl_4 could be effectively produced and volatilized from off-grade sponge and Ti-6Al-4V alloy. It was also confirmed that Fe and Ni in the Ti scrap remain in the molten salt as metal, whereas the Al and V in Ti alloy are chlorinated by SmCl_3 and their chlorides volatilized. Oxygen introduced into the reaction system was found to form TiOCl in the molten salt, and therefore does not consume the SmCl_3 mediator in the molten salt. These findings confirm that chlorination using a reaction-mediating molten salt is an effective means of recycling both titanium scrap and FeCl_x waste. [doi:10.2320/matertrans.M-M2016818]

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1. Introduction

The increasing demand for metallic titanium (Ti) and its alloys has made the recycling of Ti metal scraps a more attractive prospect than before. At present, metallic Ti is commercially produced from a titanium oxide (TiO_2) feed by the Kroll process,¹⁾ in which major impurities such as oxygen (O), iron (Fe), and aluminum (Al) can be effectively removed through the carbo-chlorination of the TiO_2 feed and subsequent purification of the titanium tetrachloride (TiCl_4) produced. The magnesiothermic reduction of TiCl_4 used to produce Ti sponge is, however, a slow, batch-type process that offers a low productivity. Furthermore, because the reduction of TiCl_4 is conducted in a steel chamber at high temperatures of around 1100 K, metallic elements that make up the inner wall of chamber such as Fe and nickel (Ni) tend to contaminate some of the Ti sponge produced. The contamination level varies depending on the size and material composition of the reduction chamber, as well as the location of the Ti deposit. However, as shown in Fig. 1(a), as much as 10–20% of the sponge produced becomes off-grade, making the majority of it unsuitable for use as a feedstock for ingots of pure Ti or Ti alloy.^{2,3)}

A significant quantity of Ti scrap is also generated during the working and machining of ingots to produce final products. Currently, the aerospace industry is the largest consumer of milled Ti product and accounts for approximately 40–50% of global demand;^{4,5)} a demand in the aerospace industry is expected to steadily increase in the foreseeable future.^{6,7)} It has been reported that 80–90% of the Ti material used in airframes is Ti-6Al-4V alloy (Ti alloyed with 6% Al and 4% vanadium (V)),^{8,9)} and as shown in Fig. 1(b), the material yield in the fabrication of aerospace parts is often as low as 10–20%.^{5,9)}

Fig. 1 Material flow in (a) Ti sponge production^{2,3)} and (b) aerospace parts fabrication.^{5,9)}

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In order to reduce the cost of producing Ti products, Ti scraps must be converted into ingots of Ti or its alloys. Re-melting is the simplest and most widely used method of forming ingots from metal scraps. However, the use of common

melting techniques for Ti and its alloys offers very limited refining capabilities with respect to major impurities such as O and Fe species as well as typical alloying elements such as Al and V.^{10,11)} As a result, only metal scraps with relatively low levels of contamination and/or well-sorted alloy compositions can be remelted into ingots. The blending ratio of Ti scraps in the melting feedstock depends on the ingot utilization and scrap quality. On average, around 40–50% of the raw material corresponds to the Ti scrap, which originates from the ingots produced by the U.S. titanium manufacture TIMET in 2006.⁴⁾ Recently, the blending ratio of the Ti scraps used for the production of aerospace-grade ingots has been increased, owing to the generation and recycling of high-grade scraps during manufacturing of aerospace parts.

Currently, low-grade scraps, which cannot be remelted (including the off-grade sponge generated during the Kroll process), are reused as additives in the production of steel or other metals (such as Al and Cu)^{3,12)} or simply treated as non-recyclable waste. The consumption of Ti scrap in the steel and other industries comprises an inherently cascaded and dissipative use of Ti. Since the increasing demand for Ti products will undoubtedly increase the volume of the generated Ti-containing scrap in the future, an effective method for recycling low-grade scraps must be developed.

The recovery of TiCl_4 by combining Ti metal scrap with iron chloride (FeCl_x , $x = 2, 3$) waste has been proposed as an environmentally friendly recycling technique.^{13–19)} Recovery of Ti in the form of TiCl_4 is advantageous in terms of providing better control over the impurity level, and is therefore well suited to recycling low-grade Ti scrap. Furthermore, this process helps to minimize the problems associated with chloride wastes,²⁰⁾ which are commonly generated and discarded in both the Kroll process and the chloride process used for producing TiO_2 pigment.^{1,21)} In these processes, TiO_2 feeds such as synthetic rutile (about 90–95% TiO_2) and ilmenite (FeTiO_3 , about 43–65% TiO_2) are carbo-chlorinated by Cl_2 gas,^{1,22)} with a considerable amount of FeCl_x and other chloride being generated as waste. Disposal of chloride waste not only represents a loss of chlorine from these processes, but also poses a significant problem in terms of the environmental issues and the high disposal cost, particularly in Japan. The generation of chloride waste will increase markedly in the future due to a decrease in the grade of TiO_2 feed used. Furthermore, if pyrometallurgical selective chlorination is widely available to upgrade low-grade Ti ores,^{13,14,23–26)} the generation of FeCl_x waste will expand even more.

From a thermodynamic point of view, TiCl_4 gas can be extracted by reacting Ti directly with FeCl_x at around 1100 K.^{13–15)} However, the chlorination reaction based on direct physical contact between Ti and FeCl_x that is shown in Fig. 2(a) poses a number of technical problems, one of which is the inherently slow kinetics of Ti chlorination at around 1100 K.¹⁸⁾ For example, when thin Ti rods ($\phi = 1.5$ or 3.0 mm, diameter) were heated in an excess amount of molten FeCl_2 (m.p. = 950 K) at 1100 K, the chlorination of Ti stopped within a few hours and most of the Ti remained unreacted (see Fig. 8 in chapter 4). This is because Fe deposited during the process rigidly covers the surface of Ti, where it acts as a strong kinetic barrier. The high volatility of FeCl_x is also a problem when Ti scrap is directly reacted with FeCl_x waste.

Fig. 2 Reaction pathways for recovering TiCl_4 from Ti scrap and chloride waste. (a) Chlorination based on direct physical contact between Ti scrap and FeCl_x waste.^{13–15)} This direct reaction poses significant drawbacks with regards to the slow kinetics of Ti chlorination and high volatilization of FeCl_x . (b) Chlorination technique utilizing a reaction-mediating molten salt such as MgCl_2 containing SmCl_3 .^{16,17)} In this molten salt, Ti is chlorinated into TiCl_4 gas by reacting with a reaction mediator (RCl_m) (reaction (A)), with the reaction mediator then regenerated from its subchloride by FeCl_x (reaction (B)). In principle, TiCl_4 can be extracted efficiently from Ti scrap because the deposition of Fe on the Ti surface is prevented. In this study, the chlorination behavior of off-grade sponge and Ti-6Al-4V alloy as well as oxygen behavior during reaction (A) is studied.

The vapor pressures of FeCl_2 and FeCl_3 exceed 10^{-1} atm above about 1090 and 540 K, respectively (see Fig. 4 in Chapter 2). FeCl_x is easily volatilized out of the reaction system at elevated temperatures before it has a chance to react with Ti scraps.

In order to overcome the problems mentioned above, the authors previously proposed a chlorination technique that utilizes a reaction-mediating molten salt.^{16,17)} In this technique, which is shown in Fig. 2(b), the chlorination of Ti scrap by FeCl_x waste can be separated into two distinct reactions that occur in the molten salt solvent: (A) the chlorination of Ti by a reaction mediator (RCl_m) that generates TiCl_4 gas and a subchloride of the reaction mediator ($\text{RCl}_{m-\delta}$); and (B) the regeneration of the reaction mediator by FeCl_x , with solid Fe being obtained as a by-product. By alternating reactions (A) and (B), TiCl_4 can be volatilized and recovered continuously thanks to the fact that Fe deposition on the surface of the scrap is prevented. Moreover, as the activity of FeCl_x can be reduced by its dissolution in a molten salt, this technique has the added advantage of suppressing the volatilization of FeCl_x from the reaction system.

The feasibility of this chlorination technique has already been confirmed by the authors through practical experiments using molten magnesium chloride (MgCl_2 , m.p. = 987 K) containing samarium trichloride (SmCl_3 , m.p. = 950 K) as a reaction-mediating molten salt.^{16–19)} However, these previous studies used commercially pure Ti rod as the feed material. The present study therefore aims to test the feasibility of using this reaction-mediator-based chlorination technique to recycle off-grade Ti sponge and Ti-6Al-4V alloy. Particular focus is given to understanding the chlorination behavior of these materials through thermodynamic analyses and funda-

mental experiments, as well as the effect of oxygen introduced into the reaction system on Ti chlorination in the $\text{MgCl}_2\text{-SmCl}_3$ molten salt.

2. Thermodynamic Analyses

2.1 Chlorination of off-grade sponge

The major impurity in off-grade sponge is Fe that diffuses from the inner wall of a reduction chamber made of steel. When the reduction chamber is made of stainless steel, some parts of the Ti sponge also become contaminated by Ni and Cr. This section therefore analyzes the chlorination behavior of Ti sponge containing Fe, Ni and Cr using the chemical potential diagrams shown in Fig. 3. These diagrams were calculated at 1100 K using thermodynamic data²⁷⁻²⁹ based on the assumption that the activity of all chemical species is unity. In each of the diagrams, the most stable phases are represented as faces, while the phase equilibria are shown by the intersections between faces.

Figure 3(a) indicates that $\text{SmCl}_3(l)$ equilibrates with $\text{TiCl}_4(g)$ and $\text{SmCl}_2(s)$ at the potential point α . When a sufficient amount of SmCl_3 is present in the reaction system, Ti can be chlorinated by SmCl_3 according to the following reac-

tion:

$$\Delta G_{r(1)}^\circ = -140 \text{ kJ at } 1100 \text{ K}$$

$$\Delta H_{r(1)}^\circ = -137 \text{ kJ at } 1100 \text{ K}$$

where $\Delta G_{r(1)}^\circ$ and $\Delta H_{r(1)}^\circ$ are the standard Gibbs energy and the standard enthalpy of reaction (1), respectively. Above reaction is solid SmCl_2 formation, whereas the reaction system in this study is liquid SmCl_2 formation in molten salt. Therefore, the Gibbs energy change of solid/liquid transformation has to be considered. According to the literature,³⁰ the melting point of SmCl_2 is 1132 K, and its Gibbs energy of fusion has small positive value at 1100 K:

$$\Delta G_{r(2)}^\circ = 0.68 \text{ kJ at } 1100 \text{ K.}$$

$$\begin{aligned} \Delta G_{r(3)}^\circ &= \Delta G_{r(1)}^\circ + 4 \times \Delta G_{r(2)}^\circ \\ &= -137 \text{ kJ at } 1100 \text{ K} \end{aligned}$$

Consequently, even in a molten salt system, Ti in scrap is po-

Fig. 3 Chemical potential diagrams at 1100 K for the (a) Ti-Sm-Cl system,^{17,27} (b) Fe-Sm-Cl system,^{17,27,28} (c) Ni-Sm-Cl system,^{27,29} and (d) Cr-Sm-Cl system.²⁷ (a) Potential point α represents $\text{TiCl}_4/\text{SmCl}_2/\text{SmCl}_3$ eq., (b) potential point β represents $\text{Fe}/\text{SmCl}_2/\text{SmCl}_3$ eq., (c) potential point γ represents $\text{Ni}/\text{SmCl}_2/\text{SmCl}_3$ eq., and (d) potential point δ represents $\text{CrCl}_2/\text{SmCl}_2/\text{SmCl}_3$ eq.

tentially chlorinated into $\text{TiCl}_4(\text{g})$ by reacting with the SmCl_3 reaction mediator as follows:

This reaction has been experimentally demonstrated using rod samples of commercially pure Ti to occur in MgCl_2 molten salt.^{16–19)}

Figures 3(b) and 3(c) show the chemical potential diagrams calculated for the Fe-Sm-Cl system^{27,28)} and Ni-Sm-Cl system,^{27,29)} respectively. Thermodynamic calculations show that $\text{Fe}(\text{s})$ and $\text{Ni}(\text{s})$ equilibrate with both $\text{SmCl}_2(\text{s})$ and $\text{SmCl}_3(\text{l})$ at the potential point β and γ , respectively, as shown in Fig. 3(b) and Fig. 3(c). This means that neither $\text{Fe}(\text{s})$ nor $\text{Ni}(\text{s})$ can be chlorinated by $\text{SmCl}_3(\text{l})$ at 1100 K. The effects of the molten salt solvents, such as a change in activity of some chlorides upon dissolution, are not considered here. Nevertheless, Fe and Ni impurities in Ti sponge can be considered to remain in the molten salt as a solid metal without being chlorinated by the SmCl_3 reaction mediator.

The chemical potential diagram for the Cr-Sm-Cl system²⁶⁾ in Fig. 3(d) indicates that $\text{Cr}(\text{s})$ cannot coexist with $\text{SmCl}_3(\text{l})$ at 1100 K, and that $\text{CrCl}_2(\text{l})/\text{SmCl}_2(\text{s})/\text{SmCl}_3(\text{l})$ equilibrium is achieved at the potential point δ . This means that $\text{SmCl}_3(\text{l})$ chlorinates $\text{Cr}(\text{s})$ to form $\text{CrCl}_2(\text{l})$ according to the following reaction:

$$\Delta G_{\text{r}(5)}^\circ = -14.9 \text{ kJ at } 1100 \text{ K}$$

$$\Delta H_{\text{r}(5)}^\circ = -38.4 \text{ kJ at } 1100 \text{ K.}$$

As $\Delta G_{\text{r}(5)}^\circ$ is far more negative than $\Delta G_{\text{r}(2)}^\circ$, it is likely that Cr is chlorinated in a SmCl_3 -containing molten salt at 1100 K as follows:

Figure 4 shows the vapor pressures of the metal chlorides calculated using thermodynamic data.^{27,30,31)} The vapor pressure of CrCl_2 is 8.0×10^{-4} atm at 1100 K,³¹⁾ which is much lower than that of TiCl_4 and FeCl_x . Consequently, any CrCl_2 generated may accumulate in the molten salt when chlorinated at around 1100 K.

2.2 Chlorination of Ti-6Al-4V alloy

The chemical potential diagrams for the Al-Sm-Cl and V-Sm-Cl system were described in order to discuss the chlorination behavior of major alloying components in Ti-6Al-4V alloy. The diagrams shown in Fig. 5 were calculated at 1100 K using available thermodynamic data.^{27,32)}

Figure 5 shows that $\text{Al}(\text{l})$ and $\text{V}(\text{s})$ do not coexist with $\text{SmCl}_3(\text{l})$. Instead, $\text{SmCl}_3(\text{l})$ equilibrates with $\text{AlCl}_3(\text{g})$ and $\text{SmCl}_2(\text{s})$ at the potential point α in Fig. 5(a), and with $\text{VCl}_2(\text{s})$ and $\text{SmCl}_2(\text{s})$ at the potential point β in Fig. 5(b). Thus, when a sufficient amount of SmCl_3 exists in the reaction system, Al and V can be chlorinated as follows:

$$\Delta G_{\text{r}(7)}^\circ = -159 \text{ kJ at } 1100 \text{ K}$$

Fig. 4 Vapor pressures of metal chlorides as functions of reciprocal temperature.^{27,30,31)} The total pressures of the monomer and dimer are plotted for AlCl_3 , FeCl_2 , FeCl_3 , and SmCl_3 .

(a) Al-Sm-Cl system, $T = 1100 \text{ K}$

(b) V-Sm-Cl system, $T = 1100 \text{ K}$

Fig. 5 Chemical potential diagrams at 1100 K for the (a) Al-Sm-Cl system^{27,32)} and (b) V-Sm-Cl system.²⁷⁾ (a) Al does not coexist with $\text{SmCl}_3(\text{l})$. (a) Potential point α represents $\text{AlCl}_3/\text{SmCl}_2/\text{SmCl}_3$ eq., (b) potential point β represents $\text{VCl}_2/\text{SmCl}_2/\text{SmCl}_3$ eq. Neither Al nor V coexists with SmCl_3 .

$$\Delta H_{r(7)}^{\circ} = -130 \text{ kJ at } 1100 \text{ K,}$$

$$\Delta G_{r(8)}^{\circ} = -44.5 \text{ kJ at } 1100 \text{ K}$$

$$\Delta H_{r(8)}^{\circ} = -128 \text{ kJ at } 1100 \text{ K.}$$

At 1100 K, $\Delta G_{r(7)}^{\circ}$ is far more negative than the Gibbs energy of fusion of Al ($-1.9 \text{ kJ}\cdot\text{mol}^{-1}$),²⁷⁾ and $\Delta G_{r(7)}^{\circ}$ and $\Delta G_{r(8)}^{\circ}$ are far more negative than $\Delta G_{r(2)}^{\circ}$ (the Gibbs energy of fusion of SmCl_2). The effect of alloying on the activities of Al and V is not considered in Fig. 5, and the Gibbs energy of fusion of VCl_2 is unclear. Nevertheless, Al and V in Ti-6Al-4V alloy scrap are still expected to be chlorinated into $\text{AlCl}_3(\text{g})$ and $\text{VCl}_2(\text{l})$, respectively, in the molten salt system at 1100 K according to the following reactions:

As shown in Fig. 4, the vapor pressure of TiCl_4 is significantly higher than that of AlCl_3 at around 400 K. This means that fractional distillation can be used to extract TiCl_4 from the gaseous mixture of TiCl_4 and AlCl_3 generated by reactions (4) and (9). The vapor pressure of VCl_2 is as high as $9.0 \times 10^{-3} \text{ atm}$ at 1100 K, and so the VCl_2 generated by reaction (10) is expected to evaporate from the molten salt.

2.3 Oxygen behavior

Since Ti scrap is often contaminated with oxygen, the behavior of oxygen introduced into the $\text{MgCl}_2\text{-SmCl}_3$ molten salt reaction system was analyzed. In Fig. 6, the chemical potential diagrams of the Ti-Cl-O, Sm-Cl-O, and Mg-Cl-O systems calculated at 1100 K are described using the logarithms of the partial pressure of chlorine (p_{Cl_2}) and partial pressure of oxygen (p_{O_2}) as the abscissa and ordinate, respectively. Figure 6(a) is constructed by overlapping the chemical potential diagram of the Ti-O-Cl system^{27,33)} and that of the Sm-O-Cl system,^{27,34)} while Fig. 6(b) is constructed by overlapping the chemical potential diagram of the Ti-O-Cl system and that of the Mg-O-Cl system.²⁷⁾ These figures show that Ti, Sm, and Mg form various oxides and/or oxychlorides depending on both p_{Cl_2} and p_{O_2} .

During the chlorination of Ti scrap by SmCl_3 , the outermost surface is controlled by the Ti/TiCl_2 equilibrium in the molten salt. When an excess amount of SmCl_3 exists in the reaction system, and when Ti scrap is completely chlorinated to TiCl_4 , the p_{Cl_2} of the reaction system is determined by the $\text{SmCl}_2/\text{SmCl}_3$ equilibrium in the molten salt. The solid line (i) and dashed line (ii) in Fig. 6 represent the p_{Cl_2} determined from the $\text{Ti(s)}/\text{TiCl}_2(\text{s})$ and $\text{SmCl}_2(\text{s})/\text{SmCl}_3(\text{l})$ equilibria, respectively. Even though the potential diagrams were described by assuming that the activity of all chemical species is unity, and by neglecting mutual solubility, it is reasonable to assume that the p_{Cl_2} in the reaction system remains between these two lines during Ti chlorination.

Under the $\text{Ti(s)}/\text{TiCl}_2(\text{s})$ equilibrium (corresponding to the solid potential line denoted by (i): $p_{\text{Cl}_2} = 7 \times 10^{-17} \text{ atm}$ and

Fig. 6 Chemical potential diagrams at 1100 K constructed by (a) overlapping the chemical potential diagram of the Ti-O-Cl system^{27,33)} and that of the Sm-O-Cl system^{27,34)} and (b) overlapping the chemical potential diagram of the Ti-O-Cl system and that of the Mg-O-Cl system.²⁷⁾ Solid line (i) and dashed line (ii) represent the p_{Cl_2} as determined by the Ti/TiCl_2 eq. and $\text{SmCl}_2/\text{SmCl}_3$ eq., respectively. Dotted lines correspond to the p_{O_2} under C/CO eq. and CO/CO_2 eq.

$p_{\text{O}_2} \leq 3 \times 10^{-42} \text{ atm}$), SmCl_2 and MgCl_2 are thermodynamically stable, whereas SmOCl , Sm_2O_3 , and MgO are unstable. Thus, when metallic Ti remains in the molten salt reaction system, SmOCl , Sm_2O_3 , and MgO are not produced during chlorination from the equilibrium point of view. Under such conditions, i.e., when metallic Ti is present ($p_{\text{O}_2} \leq 3 \times 10^{-42} \text{ atm}$), the oxygen species introduced into the reaction system are expected to form Ti-O solid solution or TiO in the molten salt, and thus do not consume the SmCl_3 reaction mediator.

Under the $\text{SmCl}_2(\text{s})/\text{SmCl}_3(\text{l})$ equilibrium (the dashed potential line marked as (ii) at $p_{\text{Cl}_2} = 2 \times 10^{-12} \text{ atm}$), the p_{O_2} range in which TiOCl is stable ($2 \times 10^{-31} \text{ atm} < p_{\text{O}_2} < 3 \times 10^{-28} \text{ atm}$) is lower than the p_{O_2} determined by the $\text{SmCl}_3(\text{l})/$

SmOCl(*s*) equilibrium ($p_{\text{O}_2} = 9 \times 10^{-28}$ atm) and MgCl₂(*l*)/MgO(*s*) equilibrium ($p_{\text{O}_2} = 6 \times 10^{-25}$ atm). This indicates that both TiOCl(*s*) and TiCl₄(*g*) are thermodynamically stable species under the SmCl₂/SmCl₃ equilibrium. The vapor pressures of TiOCl at 1100 K is calculated to be 4.2×10^{-16} atm.³³⁾ Thus, Fig. 6 indicates that oxygen introduced into the reaction system preferentially forms TiOCl in the molten salt rather than SmOCl or MgO. However, the thermodynamic data used in calculating Fig. 6, especially that for TiOCl³³⁾ and SmOCl,³⁴⁾ includes uncertainties. Under the SmCl₂(*s*)/SmCl₃(*l*) equilibrium, the difference in p_{O_2} between the SmCl₃(*l*)/SmOCl(*s*) equilibrium ($p_{\text{O}_2} = 9 \times 10^{-28}$ atm) and TiOCl(*s*)/Ti₃O₅(*s*) equilibrium ($p_{\text{O}_2} = 3 \times 10^{-28}$ atm) is small. Furthermore, as the reaction proceeds in MgCl₂-SmCl₃ molten salt, oxygen may form SmOCl or MgO kinetically. The behavior of oxygen under these conditions is experimentally examined in the following chapters (see Chapter 3 and Section 4.2).

As indicated in Fig. 6, p_{O_2} under the C(*s*)/CO(*g*) equilibrium (represented as a dotted line) is much higher than the p_{O_2}

range for TiO or TiOCl in equilibrium with Ti chlorides. This means that the removal of oxygen as CO(*g*) or CO₂(*g*) is impossible at 1100 K, even under a carbon-saturated atmosphere.

3. Experimental

Table 1 lists the materials used in this study, and Table 2 presents representative experimental conditions. Specific details regarding the experimental procedure and apparatus used is described elsewhere.¹⁷⁾ Off-grade sponge (2–5 mm granule size; contaminated with Fe, Ni, and Cr), Ti-6Al-4V alloy rod ($\phi = 1.5$ mm, diameter; $l = 36$ mm, length), or pure Ti rod ($\phi = 3.0$ mm, diameter; $l = 10$ mm, length) was placed in a carbon crucible ($\phi = 24$ mm, I.D.; $d = 70$ mm, depth) with MgCl₂-50 mol% SmCl₃ mixed salt prepared by melting a mixture of MgCl₂ and SmCl₃. In all experiments, the molar ratio of SmCl₃ to Ti used in the feed was about 6, which means that about 1.5 times more SmCl₃ was loaded than the stoichiometric amount defined by reaction (4). In Exp_71,

Table 1 Materials used in this study.

Material	Form	Purity or conc. (mass%)	Supplier
Off-grade sponge	Granule (2–5 mm)	Ti: 73 ^a Fe: 22 ^a Ni: 2 ^a Cr: 3 ^a	Toho Titanium Co., Ltd.
Ti-6Al-4V alloy	Rod ($\phi 1.5$ mm)	Ti: 89.5 Al: 6.3 V: 4.0	T and I Co., Ltd.
Commercially pure Ti	Rod ($\phi 3.0$ mm)	Ti: 99.5	The Nilaco Corporation
SmCl ₃	Powder	99.9	Strem Chemicals, Inc.
MgCl ₂	Flake	$\geq 97.0^b$	Wako Pure Chemical Industries, Ltd.
MgO	Powder	≥ 98.0	Kanto Chemical Co., Inc.

a: Analyzed by XRF. Value excluding carbon and gaseous elements.

b: Major impurity is absorbed water.

Table 2 Experimental conditions.

Exp. no.	Feed material ^a						Heat treatment ^b		Note
	Ti scrap sample			MgCl ₂ -SmCl ₃ mixed salt		MgO	Temp., T/K	Time, t'/h	
	Type	Mass, w _{sample} /g	Mass of Ti, w _{Ti,feed} /g	Mass of SmCl ₃ , w _{SmCl3} /g	Mass of MgCl ₂ , w _{MgCl2} /g	Mass, w _{MgO} /g			
Exp_74	Off-grade sponge	0.300	0.219	9.655	3.580	—	1100	6	This study
Exp_76	Ti-6Al-4V alloy rod	0.279	0.250	8.979	3.330	—	1100	6	
Exp_71	Pure Ti rod	0.311	0.309	10.02	3.714	0.077	1100	1	
Exp_63	Pure Ti rod	0.389	0.387	12.53	4.647	—	1100	1	Ref. 17)
Exp_68		0.318	0.316	10.22	3.790	—	1100	3	Ref. 19)
Exp_75		0.308	0.306	9.899	3.672	—	1100	3	Ref. 18)
Exp_69		0.310	0.308	9.987	3.704	—	1100	6	Ref. 19)
Exp_73		0.304	0.302	9.784	3.628	—	1100	6	Ref. 19)

a: Mass of Ti ($w_{\text{Ti,feed}}$) is calculated based on the mass (w_{sample}) and composition of the Ti scrap sample.

Molar ratio of SmCl₃/Ti, $X_{\text{SmCl}_3/\text{Ti}}$ ($X_{\text{SmCl}_3/\text{Ti}} = (w_{\text{SmCl}_3}/256.8)/(w_{\text{Ti,feed}}/47.87)$), was about 6.0.

b: Feed materials were heated in a carbon crucible under an Ar atmosphere.

Details of the experimental procedure and apparatus are described elsewhere.¹⁷⁾

MgO powder was also loaded in the crucible with a MgO to Ti molar ratio of 0.3 in order to deliberately introduce oxygen into the reaction system. The crucible containing the samples was positioned at the bottom of a vertical gas-tight reaction chamber, and was then held at 1100 K for 1 or 6 h under a high-purity Ar atmosphere (cf. Fig. 8 in Ref. 17)). During heat treatment, the TiCl_4 gas generated from the crucible diffused upward according to the temperature gradient in the vertical reaction chamber, where it could then be delivered out of the reaction chamber by the Ar current.

Following heat treatment, the reaction product in the carbon crucible was collected and crushed inside a glove box. The crystalline phases were identified by X-ray diffraction (XRD: Bruker Corporation, D2 PHASER, Cu-K α radiation) using a gas-tight sample holder to avoid unwanted reaction with moisture in the air. The composition of the reaction product was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES: SII NanoTechnology Inc., SPS3520UV), X-ray fluorescence spectroscopy (XRF: JEOL Co., Ltd., JSX-3100RII), and chlorine titration with silver nitrate using a dilute potassium chromate solution as the indicator. The volatilization rate of Ti ($r_{\text{Ti,volatile}}(\%)$) was calculated using the mass (w_{salt}/g) and Ti concentration ($C_{\text{Ti,salt}}(\text{mass}\%)$) of the reaction product, combined with the mass of Ti in the feed material ($w_{\text{Ti,feed}}/\text{g}$ in Table 2), as follows:

$$r_{\text{Ti,volatile}} = 100 \times (w_{\text{Ti,feed}} - w_{\text{salt}} \times C_{\text{Ti,salt}}/100)/w_{\text{Ti,feed}} \quad (11)$$

When off-grade sponge was used as the Ti scrap sample (Exp_74), a portion of the reaction product was immersed in ethanol, 50 vol% acetic acid, and then distilled water to remove any salt. A magnetic substance in the leaching residue was collected by a magnet, and was then characterized by XRD and XRF analysis. In case oxygen was introduced by adding MgO (Exp_71), a portion of the reaction product in the crucible was subjected to leaching with ethanol and 1 M hydrochloric acid. After rinsing with distilled water, ethanol and then acetone, the leaching residue was dried in air and characterized by XRD and XRF.

4. Results and Discussion

4.1 Chlorination of off-grade sponge and Ti-6Al-4V alloy by a reaction-mediating molten salt

The off-grade sponge (Exp_74) and Ti-6Al-4V alloy rod (Exp_76) disappeared when heated in MgCl_2 - SmCl_3 molten salt at 1100 K, and violet-colored reaction products were recovered from the crucible. As shown in Fig. 7, these reaction products consisted mainly of MgCl_2 and Sm_3Cl_7 . The latter is a double salt of SmCl_3 and SmCl_2 with a molar ratio of 1:2, and this is stable below 899 K.³⁵⁾ The presence of Sm_3Cl_7 in the reaction products indicates that SmCl_3 does indeed act as a chlorinating agent, with SmCl_2 being generated during heat treatment.

Table 3 summarizes the composition of the reaction products and estimated volatilization rates of Ti; results obtained by heating a commercially pure Ti rod ($\phi = 3.0$ mm) in MgCl_2 - SmCl_3 molten salt at 1100 K^{19–21)} are also shown for reference. Figure 8 shows the volatilization rate of Ti as a function of the heat treatment time, along with the reaction rate of pure Ti rod ($\phi = 1.5$ or 3.0 mm) heated in an excess of

Fig. 7 XRD profiles of reaction products recovered from the carbon crucible after heat treatment using either (a) off-grade sponge (Exp_74) or (b) Ti-6Al-4V alloy rod (Exp_76) as the Ti scrap sample.

molten FeCl_2 at 1100 K.¹⁸⁾ When the pure Ti rod was chlorinated by directly reacting with FeCl_2 at 1100 K, the reaction virtually stopped within a few hours, and a mostly unreacted Ti rod covered with Fe was obtained. When the off-grade sponge sample (Exp_74) and Ti-6Al-4V alloy rod (Exp_76) were heated in MgCl_2 - SmCl_3 molten salt at 1100 K for 6 h, on the other hand, 48 and 62% of the Ti in each respective sample was volatilized as TiCl_4 or a similar volatile compound. These volatilization rates were somewhat lower than those observed when heating pure Ti rods under the same conditions. Nevertheless, it was demonstrated that it is possible to effectively volatilize and recover Ti from off-grade sponge and Ti-6Al-4V alloy by heating in MgCl_2 - SmCl_3 molten salt in accordance with reaction (4). Figure 8 also reveals that the volatilization rate of Ti increases with heat treatment time when pure Ti rod is heated in MgCl_2 - SmCl_3 molten salt. This suggests that Ti remaining in the molten salt during Exp_74 and Exp_76 mainly forms a transient subchloride species during chlorination into TiCl_4 .

When off-grade sponge was used as the Ti scrap sample (Exp_74), the reaction product recovered from the crucible was found to attach to a magnet. As shown in Fig. 9, the diffraction peaks of the magnetic substance collected from this reaction product were identical to those of α -Fe (or Ni-dissolved α -Fe). Subsequent XRF analysis of the magnetic substance revealed a Ni to Fe mass ratio of about 0.1, which is in good agreement with that of the off-grade sponge sample. It can therefore be concluded that Fe and Ni impurities in Ti scrap remain in the molten salt as a solid metal, as was thermodynamically predicted in section 2.1. It was also thermodynamically predicted that Cr impurities would be chlorinated into CrCl_2 through the reaction (6); however, CrCl_2 was not detected by XRF of the reaction product recovered from the crucible. This is probably because the CrCl_2 content was

Table 3 Composition of the reaction product in the crucible and volatilization rate of Ti.

Exp. no.	Ti scrap sample	Reaction product recovered from the crucible							Volatilization rate of Ti, $r_{\text{Ti,volatile}}$ (%) ^d	Note
		Mass, w_{salt}/g	Composition of element i , $C_{i,\text{salt}}$ (mass%)							
			Ti ^a	Sm ^a	Mg ^a	Al ^a	V ^a	Cl ^b		
Exp_74	Off-grade sponge	12.24	0.93	44	6.8	N.D.	N.D.	44	48 ± 6	This study
Exp_76	Ti-6Al-4V alloy rod	11.52	0.85	42	6.8	(0.005)	0.009	45	61 ± 4	This study
Exp_71	Pure Ti rod	13.48	2.0	39	8.8	n.a.	n.a.	49	14 ± 9	This study MgO was also loaded.
Exp_63	Pure Ti rod	16.92	1.3	47	6.0	n.a.	n.a.	46 ^c	44 ± 6	Ref. 17)
Exp_68		13.35	1.4	38	8.2	n.a.	n.a.	47	43 ± 6	Ref. 19)
Exp_75		11.90	0.72	44	7.1	N.D.	N.D.	48	73 ± 3	Ref. 18)
Exp_69		12.78	0.39	43	7.9	n.a.	n.a.	47	84 ± 2	Ref. 19)
Exp_73		12.64	0.85	42	6.0	n.a.	n.a.	46	64 ± 4	Ref. 19)

a: Analyzed by ICP-AES. The uncertainty of the analytical value for Ti ($C_{\text{Ti,salt}}$) was within 10%.

Value in parentheses includes large uncertainty

b: Analyzed by titration with silver nitrate.

c: $C_{\text{Cl,salt}} = 100 - (C_{\text{Ti,salt}} + C_{\text{Sm,salt}} + C_{\text{Mg,salt}})$.

d: $r_{\text{Ti,volatile}} = 100 - w_{\text{salt}} \times C_{\text{Ti,salt}} / w_{\text{Ti,feed}}$. The uncertainty of $r_{\text{Ti,volatile}}$ results from the uncertainty of $C_{\text{Ti,salt}}$.

N.D.: Not detected (<0.001 mass%).

n.a.: Not analyzed.

Fig. 8 Volatilization rate of Ti when an off-grade sponge sample, Ti-6Al-4V alloy rod, and Ti rod were heated in $\text{MgCl}_2\text{-SmCl}_3$ molten salt at 1100 K. A portion of the original Ti remained in the salt even though the Ti scrap sample completely disappeared after heat treatment in each case. As a reference, the reaction rate of Ti when a Ti rod is heated in molten FeCl_2 is also shown.¹⁸⁾ When heated in molten FeCl_2 , Fe-covered Ti rods were recovered and most of the Ti remained unreacted.

too small to be identified by XRF, or because CrCl_2 was volatilized as CrCl_2 gas or another volatile compound. Further study is needed to better understand the behavior of Cr.

As shown in Table 3, the reaction product obtained by heating Ti-6Al-4V alloy rod in $\text{MgCl}_2\text{-SmCl}_3$ molten salt (Exp_76) contained only a small quantity of Al and V. Based on the mass and composition of this material, it can be said that almost all of the Al in the original sample was volatilized

Fig. 9 XRD profile of the magnetic substance collected from the reaction product in Exp_74, in which off-grade sponge was chlorinated by $\text{MgCl}_2\text{-SmCl}_3$ molten salt.

through reaction (9). Meanwhile, the V in the Ti-6Al-4V alloy rod was chlorinated into VCl_2 by SmCl_3 according to reaction (10), and then approximately 91% of the V was volatilized as VCl_2 or related volatile compounds, as discussed in section 2.2.

The experimental results presented in this section prove that TiCl_4 gas can be effectively extracted from off-grade sponge and Ti-6Al-4V alloy through chlorination using a molten salt containing SmCl_3 . In a previous study,¹⁶⁻¹⁸⁾ the authors demonstrated that SmCl_3 consumed in molten MgCl_2 can be efficiently regenerated by reacting with FeCl_x . This means that chlorination using a reaction-mediating molten

Fig. 10 XRD profiles of (a) the reaction product in the crucible and (b) its leaching residue obtained in Exp_71 where MgO powder was added in the molten salt.

salt (as shown in Fig. 2(b)) is an effective means of recycling off-grade sponge and Ti-6Al-4V alloy scraps.

4.2 Behavior of oxygen during Ti chlorination by a reaction-mediating molten salt

In Exp_71, oxygen was deliberately introduced to the reaction system by adding MgO. Though the Ti rod in the crucible disappeared after heat treatment at 1100 K for 1 h, Table 3 and Fig. 8 shows that only 14% of the Ti was volatilized. In contrast, 44% of the Ti was volatilized when a MgO-free molten salt was used under the same conditions (Exp_63).¹⁷⁾

The XRD pattern of the reaction product obtained in Exp_71 that is shown in Fig. 10(a) reveals the presence of MgCl_2 , SmCl_3 , and Sm_3Cl_7 ; the presence of the latter indicates that SmCl_3 acted as a chlorinating agent for the Ti rod. The XRD pattern also suggests that the reaction product contains TiOCl . Figure 10(b) shows the XRD pattern of the leaching residue formed from this reaction product, which shows that the residue was mostly Ti_2O_3 with a small amount of TiOCl .³⁶⁾ The Ti_2O_3 in the leaching residue should be formed by the following hydrolysis reaction during leaching: $2\text{TiOCl}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ti}_2\text{O}_3(s) + 2\text{HCl}(aq.)$. Analysis of the leaching residue by XRF did not detect the Sm-based components such as SmOCl .

The results presented in this section indicate that oxygen introduced into the reaction system formed non-volatile TiOCl and did not consume SmCl_3 when Ti was chlorinated by MgCl_2 - SmCl_3 molten salt at 1100 K. This result agrees with the thermodynamic consideration presented in section 2.3 and confirms that chlorination using a MgCl_2 - SmCl_3 molten salt is a useful way of processing Ti scrap containing oxygen as an impurity.

5. Conclusion

The chlorination behavior of Ti metal scraps when heated in SmCl_3 -containing molten MgCl_2 was investigated in order to demonstrate the viability of reaction-mediator-based chlorination for recycling both Ti scrap and FeCl_x waste. Through a combination of thermodynamic analysis and fundamental experiments, it has been demonstrated that the Ti component of off-grade Ti sponge and Ti-6Al-4V alloy can be effectively chlorinated and volatilized through reaction with SmCl_3 in the molten salt at 1100 K. It was also confirmed that Fe and Ni in off-grade sponge are not chlorinated, but rather remain as metal in the molten salt. In contrast, the Al and V in Ti-6Al-4V alloy are chlorinated by SmCl_3 and volatilized. Oxygen introduced into the reaction system was found to form TiOCl during chlorination by MgCl_2 - SmCl_3 molten salt. These findings indicate that chlorination using a reaction-mediating molten salt is a viable way of recycling not only off-grade Ti sponge generated in Ti smelters, but also Ti-6Al-4V alloy scraps such as turnings generated in metal processing factories.

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