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 FeClx (x = 2, 3) waste, the chlorination-volatilization of titanium metal scraps utilizing a MgCl2-SmCl3 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 MgCl2-SmCl3 molten salt. The results indicated that TiCl4 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 SmCl3 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 SmCl3 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 FeClx waste.

Keywords: titanium, titanium alloy, recycling, chlorination, volatilization, molten salt

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 (TiO2) 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 TiO2 feed and subsequent purification of the titanium tetrachloride (TiCl4) produced. The magnesiothermic reduction of TiCl4 used to produce Ti sponge is, however, a slow, batch-type process that offers a low productivity. Furthermore, because the reduction of TiCl4 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 air-frames 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)

In order to reduce the cost of producing Ti products, Ti scraps must be converted into ingots of Ti or its alloys. Remelting 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. 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 manufacturer TIMET in 2006. 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) 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 TiCl₄ by combining Ti metal scrap with iron chloride (FeClₓ, x = 2, 3) waste has been proposed as an environmentally friendly recycling technique. Recovery of Ti in the form of TiCl₄ 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, which are commonly generated and discarded in both the Kroll process and the chloride process used for producing TiO₂ pigment. In these processes, TiO₂ feeds such as synthetic rutile (about 90–95% TiO₂) and ilmenite (FeTiO₃, about 43–65% TiO₂) are carbo-chlorinated by Cl₂ gas, with a considerable amount of FeCl₄ 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 TiO₂ feed used. Furthermore, if pyrometallurgical selective chlorination is widely available to upgrade low-grade Ti ores, the generation of FeCl₄ waste will expand even more.

From a thermodynamic point of view, TiCl₄ gas can be extracted by reacting Ti directly with FeClₓ, at around 1100 K. However, the chlorination reaction based on direct physical contact between Ti and FeClₓ, 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. For example, when thin Ti rods (ϕ = 1.5 or 3.0 mm, diameter) were heated in an excess amount of molten FeCl₂ (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 FeClₓ is also a problem when Ti scrap is directly reacted with FeClₓ waste.

The feasibility of this chlorination technique has already been confirmed by the authors through practical experiments using molten magnesium chloride (MgCl₂, m.p. = 987 K) containing samarium trichloride (SmCl₃, m.p. = 950 K) as a reaction-mediating molten salt. 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 MgCl₂-SmCl₃ 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 data 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 SmCl₃(l) equilibrates with TiCl₄(g) and SmCl₂(s) at the potential point α. When a sufficient amount of SmCl₃ is present in the reaction system, Ti can be chlorinated by SmCl₃ according to the following reaction:

\[
\text{Ti(s)} + 4\text{SmCl}_3(l) \rightarrow \text{TiCl}_4(g) + 4\text{SmCl}_2(s) \tag{1}
\]

\[\Delta G_{r}^{\circ}(1) = -140 \text{ kJ at 1100 K}\]
\[\Delta H_{r}^{\circ}(1) = -137 \text{ kJ at 1100 K}\]

where \(\Delta G_{r}^{\circ}(1)\) and \(\Delta H_{r}^{\circ}(1)\) are the standard Gibbs energy and the standard enthalpy of reaction (1), respectively. Above reaction is solid SmCl₂ formation, whereas the reaction system in this study is liquid SmCl₂ formation in molten salt. Therefore, the Gibbs energy change of solid/liquid transformation has to be considered. According to the literature, the melting point of SmCl₂ is 1132 K, and its Gibbs energy of fusion has small positive value at 1100 K:

\[
\text{SmCl}_2(s) \rightarrow \text{SmCl}_2(l) \tag{2}
\]
\[\Delta G_{r}^{\circ}(2) = 0.68 \text{ kJ at 1100 K}\]

\[
\text{Ti(s)} + 4\text{SmCl}_3(l) \rightarrow \text{TiCl}_4(g) + 4\text{SmCl}_2(l) \tag{3}
\]
\[\Delta G_{r}^{\circ}(3) = \Delta G_{r}^{\circ}(1) + 4 \times \Delta G_{r}^{\circ}(2) = -137 \text{ kJ at 1100 K}\]

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

![Chemical potential diagrams at 1100 K](image)

Fig. 3 Chemical potential diagrams at 1100 K for the (a) Ti-Sm-Cl system, (b) Fe-Sm-Cl system, (c) Ni-Sm-Cl system, and (d) Cr-Sm-Cl system. (a) Potential point α represents TiCl₄/SmCl₂/SmCl₃ eq., (b) potential point β represents Fe/SmCl₂/SmCl₃ eq., (c) potential point γ represents Ni/SmCl₂/SmCl₃ eq., and (d) potential point δ represents CrCl₂/SmCl₂/SmCl₃ eq.
tentially chlorinated into TiCl₄(g) by reacting with the SmCl₃ reaction mediator as follows:

\[
\text{Ti(s, in scrap) + 4SmCl}_3(l, \text{in molten salt}) \rightarrow \text{TiCl}_4(g) + 4\text{SmCl}_2(l, \text{in molten salt})
\] (4)

This reaction has been experimentally demonstrated using rod samples of commercially pure Ti to occur in MgCl₂ molten salt.16–19)

Figures 3(b) and 3(c) show the chemical potential diagrams calculated for the Fe-Sm-Cl system27,28) and Ni-Sm-Cl system, respectively. Thermodynamic calculations show that Fe(s) and Ni(s) equilibrate with both SmCl₂(s) and SmCl₃(l) at the potential point β and γ, respectively, as shown in Fig. 3(b) and Fig. 3(c). This means that neither Fe(s) nor Ni(s) can be chlorinated by SmCl₃(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.

The chemical potential diagram for the Cr-Sm-Cl system26) in Fig. 3(d) indicates that Cr(s) cannot coexist with SmCl₃(l) at 1100 K, and that CrCl₂(l)/SmCl₂(s)/SmCl₃(l) equilibrium is achieved at the potential point δ. This means that SmCl₃(l) chlorinates Cr(s) to form CrCl₂(l) according to the following reaction:

\[
\text{Cr(s)} + 2\text{SmCl}_3(l) \rightarrow \text{CrCl}_2(l) + 2\text{SmCl}_2(s)
\] (5)

\[
\Delta G_{r}^{\circ}(5) = -159 \text{ kJ at 1100 K}
\]

As \(\Delta G_{r}^{\circ}(5)\) is far more negative than \(\Delta G_{r}^{\circ}(2)\), it is likely that Cr is chlorinated in a SmCl₃-containing molten salt at 1100 K as follows:

\[
\text{Cr(s, in scrap) + 2SmCl}_3(l, \text{in molten salt}) \rightarrow \text{CrCl}_2(l, \text{in molten salt}) + 2\text{SmCl}_2(l, \text{in molten salt})
\] (6)

Figure 4 shows the vapor pressures of the metal chlorides calculated using thermodynamic data.27,30,31) The vapor pressure of CrCl₂ is 8.0 × 10⁻⁴ atm at 1100 K,31) which is much lower than that of TiCl₄ and FeCl₃. Consequently, any CrCl₂ 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 Al(l) and V(s) do not coexist with SmCl₃(l). Instead, SmCl₃(l) equilibrates with AlCl₃(g) and SmCl₂(s) at the potential point α in Fig. 5(a), and with VCl₂(s) and SmCl₂(s) at the potential point β in Fig. 5(b). Thus, when a sufficient amount of SmCl₃ exists in the reaction system, Al and V can be chlorinated as follows:

\[
\text{Al(l) + 3SmCl}_3(l) \rightarrow \text{AlCl}_3(g) + 3\text{SmCl}_2(s)
\] (7)

\[
\Delta G_{r}^{\circ}(7) = -159 \text{ kJ at 1100 K}
\]
\[ \Delta H^0_{f, \text{Ti}(s)} = -130 \text{kJ at 1100 K}, \]

\[ V(s) + 2\text{SmCl}_3(l) \rightarrow \text{VCl}_2(s) + 2\text{SmCl}_2(s) \quad (8) \]

\[ \Delta G^0_{f,(8)} = -44.5 \text{kJ at 1100 K} \]

\[ \Delta H^0_{f,(8)} = -128 \text{kJ at 1100 K}. \]

At 1100 K, \( \Delta G^0_{f,(7)} \) is far more negative than the Gibbs energy of fusion of Al (\(-1.9 \text{kJ mol}^{-1}\)), \( \Delta G^0_{f,(7)} \) and \( \Delta G^0_{f,(8)} \) are far more negative than \( \Delta G^0_{f,(2)} \) (the Gibbs energy of fusion of SmCl3). The effect of alloying on the activities of Al and V is not considered in Fig. 5, and the Gibbs energy of fusion of VCl2 is unclear. Nevertheless, Al and V in Ti-6Al-4V alloy scrap are still expected to be chlorinated into AlCl3 and VCl2, respectively, in the molten salt system at 1100 K according to the following reactions:

\[ \text{Al}(s, \text{in scrap}) + 3\text{SmCl}_3(l, \text{in molten salt}) \]

\[ \rightarrow 3\text{SmCl}_2(l, \text{in molten salt}) + \text{AlCl}_3(l, \text{in molten salt}) \quad (9) \]

\[ \text{V}(s, \text{in scrap}) + 2\text{SmCl}_3(l, \text{in molten salt}) \]

\[ \rightarrow \text{VCl}_2(l, \text{in molten salt}) + 2\text{SmCl}_2(l, \text{in molten salt}) \quad (10) \]

As shown in Fig. 4, the vapor pressure of TiCl4 is significantly higher than that of AlCl3 around 400 K. This means that fractional distillation can be used to extract TiCl4 from the gaseous mixture of TiCl4 and AlCl3 generated by reactions (4) and (9). The vapor pressure of VCl2 is as high as 9.0 × 10^{-10} \text{atm} at 1100 K, and so the VCl2 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 MgCl2-SmCl3 molten salt reaction system was analyzed. In Fig. 6, the chemical potential diagrams of the Ti-O-Cl, Sm-O-Cl, and Mg-O-Cl systems calculated at 1100 K are described using the logarithms of the partial pressure of chlorine (\( p_{\text{Cl}_2} \)) and partial pressure of oxygen (\( p_{\text{O}_2} \)) as the abscissa and ordinate, respectively. Figure 6(a) is constructed by overlapping the chemical potential diagram of the Ti-O-Cl system and that of the Sm-O-Cl system, 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. These figures show that Ti, Sm, and Mg form various oxides and/or oxychlorides depending on both \( p_{\text{Cl}_2} \) and \( p_{\text{O}_2} \).

During the chlorination of Ti scrap by SmCl3, the outermost surface is controlled by the Ti/TiCl4 equilibrium in the molten salt. When an excess amount of SmCl3 exists in the reaction system, and when Ti scrap is completely chlorinated to TiCl4, the \( p_{\text{Cl}_2} \) of the reaction system is determined by the SmCl2/SmCl3 equilibrium in the molten salt. The solid line (i) and dashed line (ii) in Fig. 6 represent the \( p_{\text{Cl}_2} \) determined from the Ti(s)/TiCl4(s) and SmCl2(s)/SmCl3(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 \( p_{\text{Cl}_2} \) in the reaction system remains between these two lines during Ti chlorination.

Under the Ti(s)/TiCl4(s) equilibrium (corresponding to the solid potential line denoted by (i)):\n
\[ p_{\text{Cl}_2} = 7 \times 10^{-17} \text{atm} \]

\[ p_{\text{O}_2} \leq 3 \times 10^{-42} \text{atm}, \]

SmCl2 and MgCl2 are thermodynamically stable, whereas SmOCl, SmO2, and MgO are unstable. Thus, when metallic Ti remains in the molten salt reaction system, SmOCl, Sm2O3, 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 SmCl3 reaction mediator.

Under the SmCl2(s)/SmCl3(l) equilibrium (the dashed potential line marked as (ii)) at \( p_{\text{Cl}_2} = 2 \times 10^{-12} \text{atm} \), the \( p_{\text{O}_2} \) range in which TiOC1 is stable (\( 2 \times 10^{-31} \text{atm} < p_{\text{O}_2} < 3 \times 10^{-28} \text{atm} \)) is lower than the \( p_{\text{O}_2} \) determined by the SmCl3(l)/
SmOCl(s) equilibrium ($p_{O_2} = 9 \times 10^{-28}$ atm) and MgCl$_2$(l)/MgO(s) equilibrium ($p_{O_2} = 6 \times 10^{-25}$ atm). This indicates that both TiOCl(s) and TiCl$_4$(g) are thermodynamically stable species under the SmCl$_3$/SmOCl$_2$ equilibrium. The vapor pressures of TiOCl at 1100 K is calculated to be $4.2 \times 10^{-16}$ atm. 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 TiOCl, includes uncertainties. Under the SmCl$_2$(s)/SmOCl$_2$(l) equilibrium, the difference in $p_{O_2}$ between the SmCl$_3$(l)/SmOCl(s) equilibrium ($p_{O_2} = 9 \times 10^{-28}$ atm) and TiOCl(s)/Ti$_2$O$_3$(s) equilibrium ($p_{O_2} = 3 \times 10^{-28}$ atm) is small. Furthermore, as the reaction proceeds in MgCl$_2$-SmCl$_3$ 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 CO$_2$(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. Off-grade sponge (2–5 mm granule size; contaminated with Fe, Ni, and Cr), Ti-6Al-4V alloy rod ($d = 1.5$ mm, diameter; $l = 36$ mm, length), or pure Ti rod ($d = 3.0$ mm, diameter; $l = 10$ mm, length) was placed in a carbon crucible ($d = 24$ mm, I.D.; $d = 70$ mm, depth) with MgCl$_2$-50 mol% SmCl$_3$ mixed salt prepared by melting a mixture of MgCl$_2$ and SmCl$_3$. In all experiments, the molar ratio of SmCl$_3$ to Ti used in the feed was about 6, which means that about 1.5 times more SmCl$_3$ was loaded than the stoichiometric amount defined by reaction (4). In Exp_71,

### Table 1 Materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>Purity or conc. (mass%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-grade sponge</td>
<td>Granule (2–5 mm)</td>
<td>Ti: 73\textsuperscript{a}</td>
<td>Toho Titanium Co., Ltd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe: 22\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni: 2\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr: 3\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V alloy</td>
<td>Rod ($d=1.5$ mm)</td>
<td>Ti: 89.5</td>
<td>T and I Co., Ltd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al: 6.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V: 4.0</td>
<td></td>
</tr>
<tr>
<td>Commercially pure Ti</td>
<td>Rod ($d=0.0$ mm)</td>
<td>Ti: 99.5</td>
<td>The Nilaco Corporation</td>
</tr>
<tr>
<td>SmCl$_3$</td>
<td>Powder</td>
<td>99.9</td>
<td>Stem Chemicals, Inc.</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>Flake</td>
<td>$\geq 97.0\textsuperscript{b}$</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
</tr>
<tr>
<td>MgO</td>
<td>Powder</td>
<td>$\geq 98.0$</td>
<td>Kanto Chemical Co., Inc.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Analyzed by XRF. Value excluding carbon and gaseous elements.

\textsuperscript{b} Major impurity is absorbed water.

### Table 2 Experimental conditions.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Feed material\textsuperscript{a}</th>
<th>Ti scrap sample</th>
<th>MgCl$_2$-SmCl$_3$ mixed salt</th>
<th>MgO</th>
<th>Heat treatment\textsuperscript{b}</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Mass, $w_{\text{sample}}$/g</td>
<td>Mass of Ti, $w_{\text{Ti,feed}}$/g</td>
<td>Mass of SmCl$<em>3$, $w</em>{\text{SmCl}_3}$/g</td>
<td>Mass of MgCl$<em>2$, $w</em>{\text{MgCl}_2}$/g</td>
<td>Mass, $w_{\text{MgO}}$/g</td>
</tr>
<tr>
<td>Exp_74</td>
<td>Off-grade sponge</td>
<td>0.300</td>
<td>0.219</td>
<td>9.655</td>
<td>3.580</td>
<td>—</td>
</tr>
<tr>
<td>Exp_76</td>
<td>Ti-6Al-4V alloy rod</td>
<td>0.279</td>
<td>0.250</td>
<td>8.979</td>
<td>3.330</td>
<td>—</td>
</tr>
<tr>
<td>Exp_71</td>
<td>Pure Ti rod</td>
<td>0.311</td>
<td>0.309</td>
<td>10.02</td>
<td>3.714</td>
<td>0.077</td>
</tr>
<tr>
<td>Exp_63</td>
<td>Pure Ti rod</td>
<td>0.389</td>
<td>0.387</td>
<td>12.53</td>
<td>4.647</td>
<td>—</td>
</tr>
<tr>
<td>Exp_68</td>
<td></td>
<td>0.318</td>
<td>0.316</td>
<td>10.22</td>
<td>3.790</td>
<td>—</td>
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<tr>
<td>Exp_75</td>
<td></td>
<td>0.308</td>
<td>0.306</td>
<td>9.899</td>
<td>3.672</td>
<td>—</td>
</tr>
<tr>
<td>Exp_69</td>
<td></td>
<td>0.310</td>
<td>0.308</td>
<td>9.987</td>
<td>3.704</td>
<td>—</td>
</tr>
<tr>
<td>Exp_73</td>
<td></td>
<td>0.304</td>
<td>0.302</td>
<td>9.784</td>
<td>3.628</td>
<td>—</td>
</tr>
</tbody>
</table>

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

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

\textsuperscript{b} Feed materials were heated in a carbon crucible under an Ar atmosphere.

Details of the experimental procedure and apparatus are described elsewhere.\textsuperscript{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 TiCl4 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-Kα 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 ($w_{\text{salt}}$) and Ti concentration ($C_{\text{Ti,salt}}$) of the reaction product, combined with the mass of Ti in the feed material ($w_{\text{Ti,feed}}$) in Table 2, as follows:

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

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 MgCl2-SmCl3 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 MgCl2 and Sm2Cl7. The latter is a double salt of SmCl3 and SmCl2 with a molar ratio of 1:2, and this is stable below 899 K. The presence of Sm2Cl7 in the reaction products indicates that SmCl3 does indeed act as a chlorinating agent, with SmCl2 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 MgCl2-SmCl3 molten salt at 1100 K 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 molten FeCl2 at 1100 K. When the pure Ti rod was chlorinated by directly reacting with FeCl2 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 MgCl2-SmCl3 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 TiCl4 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 MgCl2-SmCl3 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 MgCl2-SmCl3 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 TiCl4.

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 $\alpha$-Fe (or Ni-dissolved $\alpha$-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 CrCl2 through the reaction (6); however, CrCl2 was not detected by XRF of the reaction product recovered from the crucible. This is probably because the CrCl2 content was
too small to be identified by XRF, or because CrCl₂ was volatilized as CrCl₂ 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 MgCl₂-SmCl₃ 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 through reaction (9). Meanwhile, the V in the Ti-6Al-4V alloy rod was chlorinated into VCl₂ by SmCl₃ according to reaction (10), and then approximately 91% of the V was volatilized as VCl₂ or related volatile compounds, as discussed in section 2.2.

The experimental results presented in this section prove that TiCl₄ gas can be effectively extracted from off-grade sponge and Ti-6Al-4V alloy through chlorination using a molten salt containing SmCl₃. In a previous study, the authors demonstrated that SmCl₃ consumed in molten MgCl₂ can be efficiently regenerated by reacting with FeClₓ. This means that chlorination using a reaction-mediating molten

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Ti scrap sample</th>
<th>Mass, wₛalt/g</th>
<th>Composition of element i, Cᵢₛalt (mass%)</th>
<th>Volatilization rate of Ti, rᵢvolatile (%)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Note</th>
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<tr>
<td></td>
<td>Reaction product</td>
<td>Ti&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Sm&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Mg&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Al&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Exp_74</td>
<td>Off-grade sponge</td>
<td>12.24</td>
<td>0.93</td>
<td>44</td>
<td>6.8</td>
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<td>Exp_76</td>
<td>Ti-6Al-4V alloy</td>
<td>11.52</td>
<td>0.85</td>
<td>42</td>
<td>6.8 (0.005)</td>
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<td>Exp_71</td>
<td>Pure Ti rod</td>
<td>13.48</td>
<td>2.0</td>
<td>39</td>
<td>8.8</td>
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<tr>
<td>Exp_63</td>
<td>Pure Ti rod</td>
<td>16.92</td>
<td>1.3</td>
<td>47</td>
<td>6.0</td>
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<td>Exp_68</td>
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<td>13.35</td>
<td>1.4</td>
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<td>7.1</td>
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<tr>
<td>Exp_69</td>
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<td>12.78</td>
<td>0.39</td>
<td>43</td>
<td>7.9</td>
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<tr>
<td>Exp_73</td>
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<td>12.64</td>
<td>0.85</td>
<td>42</td>
<td>6.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Analyzed by ICP-AES. The uncertainty of the analytical value for Ti (C<sub>Ti,salt</sub>) was within 10%.

<sup>b</sup>: Analyzed by titration with silver nitrate.

<sup>c</sup>: C<sub>Cl,salt</sub> = 100 – (C<sub>Ti,salt</sub> + C<sub>Sm,salt</sub> + C<sub>Mg,salt</sub>).

<sup>d</sup>: rᵢvolatile = 100 – wₛalt × Cᵢₛalt/wᵢfeed. The uncertainty of rᵢvolatile results from the uncertainty of Cᵢₛalt.

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

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Fig. 8  Volatilization rate of Ti when an off-grade sponge sample, Ti-6Al-4V alloy rod, and Ti rod were heated in MgCl₂-SmCl₃ 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 FeCl₂ is also shown. When heated in molten FeCl₃, Fe-covered Ti rods were recovered and most of the Ti remained unreacted.

Fig. 9  XRD profile of the magnetic substance collected from the reaction product in Exp_74, in which off-grade sponge was chlorinated by MgCl₂-SmCl₃ 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 MgCl2, SmCl3, and Sm3Cl7; the presence of the latter indicates that SmCl3 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 obtained in Exp_71 where MgO powder was added in the molten salt.

### 5. Conclusion

The chlorination behavior of Ti metal scraps when heated in SmCl3-containing molten MgCl2 was investigated in order to demonstrate the viability of reaction-mediator-based chlorination for recycling both Ti scrap and FeCl3 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 SmCl3 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 SmCl3 and volatilized. Oxygen introduced into the reaction system was found to form TiOCl during chlorination by MgCl2-Smitholten 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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### REFERENCES