Selective Removal of Iron from Low-Grade Ti Ore by Reacting with Calcium Chloride

JUNGSHIN KANG and TORU H. OKABE

Recently, titanium metal production by molten salt electrolysis using $CaCl_2$ as molten salt and TiO_2 or rutile (94 to 96 pct TiO_2) as feedstock has been drawing attention. However, when a low-grade Ti ore (mainly $FeTiO_3$) is used as feedstock, removal of iron (Fe) from the ore is indispensable. In this study, the influence of reaction temperature, reaction time, particle size of the ore, and source country for the ore on the removal of iron by selective chlorination using $CaCl_2$ was assessed. Experimental results showed that the mass percent of iron in the ore decreased from 49.7 to 1.79 pct under certain conditions by selective removal of iron as $FeCl_2$. As a result, high-grade $CaTiO_3$ was produced when the ore particles smaller than 74 μm reacted with $CaCl_2$ at 1240 K (967 °C) for 8 to 10 hours. Therefore, this study demonstrates that the removal of iron from the ore is feasible through the selective chlorination process using $CaCl_2$ by optimizing the variables.

I. INTRODUCTION

THE Kroll process is the current commercial process for the production of Ti metal. However, the productivity of this process is low, owing to its slow production speed and batch-type processing. The FFC (Fray–Farthing–Chen),[1] the OS (Ono-Suzuki),[2] and the electronically mediated reaction/molten salt electrolysis (EMR/MSE)[3] processes have been proposed as alternatives to overcome the limitations of the Kroll process. The FFC and OS processes have been found to be promising among the new processes, because these are simple and semi-continuous processes. In the FFC or the OS process, Ti metal can be obtained directly from TiO_2 in a molten $CaCl_2$ by an electrochemical method or metallothermic method using calcium (Ca) as a reducing agent. During the electrochemical reductions in the FFC process, $CaTiO_3$ is generated as an intermediate.[4,5] This $CaTiO_3$ is eventually reduced to Ti metal, as reported by Jiang et al.[4] and Vishnu et al.[6]

Recently, Metalysis Ltd, U.K., reported an interesting result that rutile (94 to 96 pct TiO_2) can be used as a feedstock in the FFC process.[7] This indicates that the removal of Fe from ilmenite, which is the most important Ti mineral resource, is indispensable when a low-grade Ti ore (mainly $FeTiO_3$) is used in the FFC process. In the current Ti ore upgrading industry, synthetic rutile is prepared by the Becher,[8] Benilite,[9–11] or slag and UGS (Upgraded Slag)[12] process. The Becher, Benilite, and UGS processes use concentrated acid for the removal of Fe and other impurities from a low-grade Ti ore or Ti slag. As a result, acid waste solution is generated, and the treatment of this waste solution is costly in countries with stringent environmental regulations.

In 2007, Zheng[13] developed a novel method for the selective chlorination of Ti ore using $CaCl_2$ as a chlorinating agent reacting with Fe and forming $CaTiO_3$. However, the Fe in the ore was only partially removed: the mass percent of Fe decreased from 51 to 17 pct at 1293 K (1020 °C). The authors also reported that the mass percent of Fe decreased from 50 to 18 pct at 1100 K (827 °C) through the selective removal of Fe by $CaCl_2$.[14] The authors analyzed that Fe was only partially removed because $CaTiO_3$ formed at an outer layer on ore particles and impeded the reaction between Fe in the center parts of the particles and $CaCl_2$.

Even though the mechanism of the selective chlorination using $CaCl_2$ was investigated by Zheng,[13] the purity of the produced $CaTiO_3$ is not enough to be used as a feedstock for the FFC process. Therefore, this study investigated the influence of reaction temperature, reaction time, and particle size of the ore on the amount of Fe removed as $FeCl_2$ to produce high-grade $CaTiO_3$ when $CaCl_2$ was reacted with the ore through direct physical contact. High-grade $CaTiO_3$ indicates that the amount of impurities except Ca in $CaTiO_3$ are less than or equal to that of the impurities in rutile. In addition, the ores produced in several countries were used as feedstock for the verification of the feasibility of the developed selective chlorination process. However, the

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mines of the ores used were not specified although the compounds of the ores were analyzed.[15]

In this study, the iron removal ratio increased from 69 pct[14] or 82 pct[13] to 96-98 pct through the determination and the optimization of the effective experimental parameters for the selective removal of Fe from ilmenite to produce high-grade $CaTiO_3$ in molten $CaCl_2$. In addition, the amount of the feedstock was increased by two or twelve times compared to the previous study because the homogeneous chlorination reactions were difficult to achieve owing to the use of a small amount of Ti ore in the authors' previous study.[14]

Figure 1 shows the flowchart of a novel Ti metal production process. First, Fe in a low-grade Ti ore is selectively removed as $FeCl_2$ and high-grade $CaTiO_3$ is obtained by the following reaction: $FeTiO_3$ (s) + $CaCl_2$ (l) = $FeCl_2$ (l, g) + $CaTiO_3$ (s). If high-grade $CaTiO_3$ can be prepared from low-grade Ti ore by direct reaction with $CaCl_2$, concentrated acid is not required to upgrade the ore. The recyclability of the generated $FeCl_2$ has been reported in several studies.[16,17] The $CaTiO_3$ produced is used as a feedstock for the FFC process, and Ti metal is obtained.

II. EXPERIMENTAL

Figure 2 shows the schematic and a photograph of the experimental apparatus, while Table I shows the experimental conditions and analytical results for feedstocks and residues. Prior to its use, $CaCl_2$ (anhydrous; purity >95.0 pct; Kanto Chemicals, Inc.) was dried for more than 3 days at 473 K (200 °C) in a vacuum oven. To prepare the experiment, half of the total $CaCl_2$ amount and the entire amount of the ore were uniformly mixed, and placed in a molybdenum-lined nickel crucible (nickel crucible: I.D. = 36 mm; depth = 36 mm; thickness of Mo-lining = 0.1 mm). Thereafter, the remaining $CaCl_2$ was added to the mixture in the crucible. For Exp. no. 130509, the preparation was the same as described above, with the exception of the crucible, which had different dimensions (nickel crucible: I.D. = 60 mm; depth = 59 mm; thickness of Mo-lining = 0.05 mm). A top lid was loosely placed over the crucible, and the crucible was placed inside a vertical stainless steel reactor, which was then sealed with silicone rubber plugs.
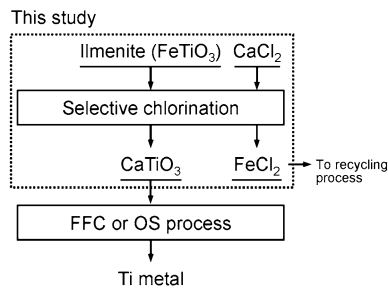
Subsequently, the reactor was evacuated twice for 10 minutes each time, and Ar gas (purity > 99.9995 pct) was flowed through the reactor until the internal pressure reached 1 atm. The internal pressure was maintained at 1 atm during the experiments. The Ar gas flow was set to 200 ml/min and controlled with a flow meter. The temperature of the reactor was increased to the target reaction temperature at a rate of 4.9 K/min.

After the completion of the reactions, the reactor was cooled to room temperature, and the residues were obtained from the crucible. The residues were dissolved in deionized water with sonication for at least 2 hours at room temperature. Then, the residues were leached in stirred 6.47 M HCl aqueous solution at room temperature for 0.5 hours. The chemical compositions of the samples were determined using X-ray fluorescence (XRF: JEOL, JSX-3100RII) spectroscopy, and their compounds were identified by X-ray diffraction (XRD: RIGAKU, RINT 2500, RINT 2000, Cu-Kα radiation) analysis.

III. RESULTS AND DISCUSSION

Figure 3(a) shows the presence of white deposits that condensed in the low-temperature regions of the reactor. These deposits were identified as $FeCl_2 \cdot (H_2O)_2$ and $FeCl_2 \cdot 4(H_2O)$ by XRD analysis, as shown in Figure 4. When the XRD analysis of the deposits was carried out, double-sided adhesive tape and polymide tape were used for the adhesion of deposits and the prevention of
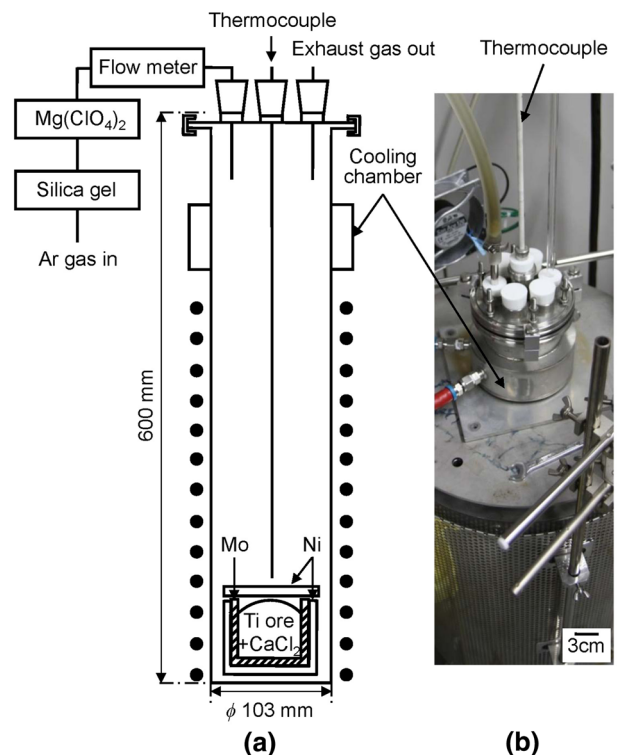

Fig. 1—Flowchart of the selective chlorination process investigated in this study.

Fig. 2—(a) Schematic of stainless steel reactor vessel and (b) photograph of reaction vessel and electric furnace.

Table I. Experimental Conditions and Analytical Results of Feedstocks and Residues Obtained After Experiments

| Exp. No.* | Source country for Ti ore | Reaction time, t_r'/h | Reaction temp., T/K (T'/°C) | Particle size of Ti ore, d_{ore}/μm | Weight of CaCl₂, w_{CaCl2}/g | Weight of Ti ore, w_{ore}/g | Mass percent of element i, C_i (mass pct)** | | | | Iron removal ratio, R_{Fe} (pct)† | Total mass percent of all elements except Ti and Ca, C_m (mass pct)‡ |
							Ti	Fe	Ca	Mn		
Feedstock	Vietnam						45.0	49.7	0.04	3.47		54.9
	Australia						48.5	46.7	0.07	1.69		51.4
	China						47.2	45.4	0.21	2.79		52.6
121022	Vietnam	10	1240 (967)	under 44	10.00	0.5	57.2	2.49	39.3	0.13	96	3.43
121024	Australia	10	1240 (967)	under 44	10.00	0.5	63.7	1.59	33.5	0.06	97	2.81
121028	China	10	1240 (967)	under 44	10.00	0.5	61.5	1.35	35.0	0.11	98	3.49
121127	Vietnam	10	1200 (927)	under 44	10.00	0.5	56.1	4.16	39.1	0.22	93	4.76
121113	Vietnam	10	1100 (827)	under 44	10.00	0.5	52.8	14.2	31.9	0.34	76	15.3
121029	Vietnam	10	1240 (967)	44–74	10.00	0.5	55.6	1.79	42.0	0.16	97	2.41
121031	Vietnam	10	1240 (967)	74–149	10.00	0.5	55.1	3.07	41.1	0.20	95	3.81
121101	Vietnam	10	1240 (967)	149–210	10.00	0.5	53.7	14.4	31.0	0.54	76	15.3
121106	Vietnam	10	1240 (967)	210–297	10.00	0.5	49.7	29.6	18.9	1.36	46	31.4
121210	Vietnam	8	1240 (967)	under 44	10.00	0.5	55.3	1.87	42.4	0.13	97	2.32
121211	Vietnam	6	1240 (967)	under 44	10.00	0.5	56.6	4.90	37.7	0.23	92	5.66
121213	Vietnam	4	1240 (967)	under 44	10.00	0.5	57.3	4.13	38.0	0.22	93	4.75
121219	Vietnam	2	1240 (967)	under 44	10.00	0.5	55.5	8.25	35.6	0.23	87	8.93
130509	Vietnam	20	1240 (967)	under 44	30.00	3.0	56.5	2.22	40.5	0.25	96	3.04

* Experimental conditions; Ar gas flow controlled by flow meter, v_{Ar} = 200 ml/min.
** Determined by XRF analysis (excluding oxygen, other gaseous elements, and elements lighter than sodium); values are determined by the average of analytical results of five samples.
† R_{Fe}(pct) $= 100 \times \{1 - (C_{Fe}^{residue}/C_{Ti}^{residue})/(C_{Fe}^{feed}/C_{Ti}^{feed})\}$, introduced by Zheng.[13]
C_{Fe}^{feed}: the mass percent of iron in the feedstock before the experiment, $C_{Fe}^{residue}$: the mass percent of iron in the residue obtained after the experiment.
C_{Ti}^{feed}: the mass percent of titanium in the feedstock before the experiment, $C_{Ti}^{residue}$: the mass percent of titanium in the residue obtained after the experiment.
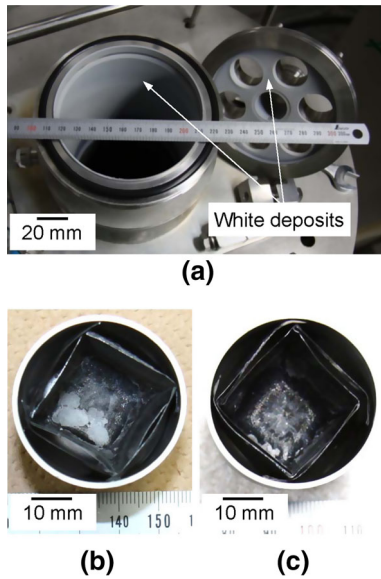‡ C_m (mass pct) $= 100 - (C_{Ti} + C_{Ca})$.

Fig. 3—Photographs of the reactor and crucible after the experiment: (*a*) white deposits at the low-temperature part of the furnace and residues in the molybdenum-lined nickel crucible; (*b*) (Exp. no. 121024) and (*c*) (Exp. no. 121101).
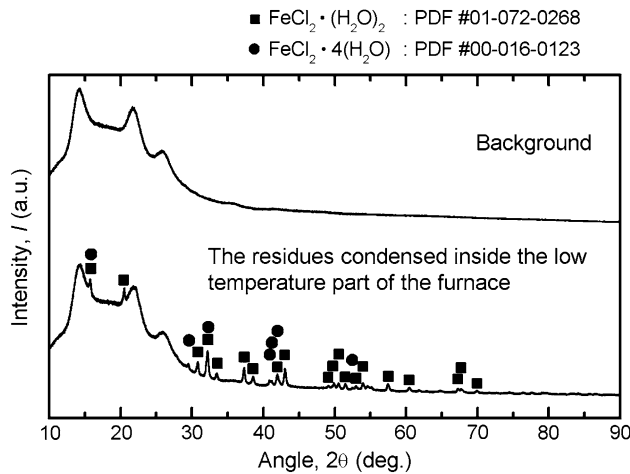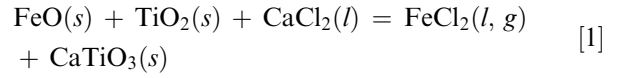

■ $FeCl_2 \cdot (H_2O)_2$: PDF #01-072-0268
● $FeCl_2 \cdot 4(H_2O)$: PDF #00-016-0123

Fig. 4—XRD results of the white deposits that condensed inside the low-temperature part of the furnace (Exp. no. 121029).

adsorption of H_2O present in air onto the deposits during analysis, respectively. The background pattern in Figure 4 was obtained when the blank XRD sample holder with this setup was analyzed. This setup was expected to prevent the adsorption of H_2O; however, the results of XRD analysis showed that H_2O was adhered to $FeCl_2$. The adherence of H_2O is expected to occur through either or both of the following routes: (1) H_2O in the air adhered to $FeCl_2$ when the top lid of the furnace was removed; (2) H_2O adhered initially to the $CaCl_2$ during the preparation of experiments and liberated when the reactor temperature was increased.

As shown in Table I, when chlorination reactions were carried out at 1240 K (967 °C) for 8 to 10 hours using ore particles smaller than 74 μm, the mass percent of Fe for feedstock decreased from 45.4-49.7 to

1.35-2.49 pct for the residues. In addition, Figures 6 and 7 show that TiO_2 and $CaTiO_3$ were obtained under the above conditions. These results show that the Fe in the ore was selectively removed as $FeCl_2$ by reacting with $CaCl_2$, according to Eq. [1] or [2][18]: The value of $\Delta G°_r$ is slightly different depending on database.

$$FeO(s) + TiO_2(s) + CaCl_2(l) = FeCl_2(l, g) \\ + CaTiO_3(s) \tag{1}$$

$$\Delta G_r^\circ = 6.1\,\text{kJ at } 1240\,\text{K}\,(967\,°\text{C})$$

$$FeTiO_3(s) + CaCl_2(l) = FeCl_2(l, g) + CaTiO_3(s) \tag{2}$$

$$\Delta G_r^\circ = 15.8\,\text{kJ at } 1240\,\text{K}\,(967\,°\text{C})$$

The generated $FeCl_2$ was removed as gas and condensed at the low-temperature regions of the furnace because the vapor pressure of $FeCl_2$ is 0.22 atm at 1240 K (967 °C) which is sufficient to evaporate.[18] In addition, when some amount of $FeCl_2$ dissolves in $CaCl_2$, the activity of $FeCl_2$ is decreased. Therefore, the Gibbs free energy of the reactions in Eqs. [1] and [2] would decrease, and chlorination reaction would proceed.

As shown in Eq. [3], when the activity of CaO (a_{CaO}) is unity, it is difficult to remove Fe in the ore with $CaCl_2$.[18] However, when a_{CaO} decreases through the formation of $CaTiO_3$ as in Eq. [4],[18] the reaction in Eq. [3] can proceed because of the decrease of ΔG_r of Eq. [3]. In addition, the high solubility of CaO in $CaCl_2$ at high temperatures also helps to decrease the activity of CaO:19.4 mol pct of CaO in $CaCl_2$ at 1173 K (900 °C).[19] The activity of FeO (a_{FeO}) by the formation of $FeTiO_3$ is 0.663 at 1240 K when the activity of both TiO_2 and $FeTiO_3$ is unity.[18] However, the a_{FeO} was assumed to be unity in this study owing to the high value of a_{FeO}. As a result, the Fe in the ore can be selectively removed as $FeCl_2$ by $CaCl_2$.

$$FeO(s) + CaCl_2(l) = FeCl_2(l, g) + CaO(s) \tag{3}$$

$$\Delta G_r^\circ = 95.3\,\text{kJ at } 1240\,\text{K}\,(967\,°\text{C})$$

$$\Delta G_r = \Delta G_r^\circ + RT \ln(p_{FeCl2} \cdot a_{CaO}/a_{FeO} \cdot a_{CaCl2})$$
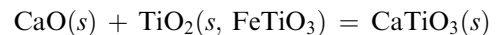
$$CaO(s) + TiO_2(s, FeTiO_3) = CaTiO_3(s)$$
$$a_{CaO} = 1.74 \times 10^{-4} \text{ at } 1240\,\text{K } (967\,°\text{C})^{[18]} \tag{4}$$
when $a_{TiO_2} = 1$ and $a_{CaTiO_3} = 1$.

The selective chlorination of Ti ore using $CaCl_2$ can also be analyzed using the combined chemical potential diagram of Fe-O-Cl and Ti-O-Cl systems at 1240 K (967 °C), shown in Figure 5.[18] When the oxygen and chlorine chemical potentials are located in the hatched region (potential region for selective chlorination), Fe in the ore can be selectively chlorinated as $FeCl_x$ (*l*, *g*, *x* = 2, 3). When the activity of CaO is unity, the CaO (*s*)/$CaCl_2$ (*l*) eq.[b] line in Figure 5 does not pass through the potential region for selective chlorination. However, when the activity of CaO decreases by the formation of
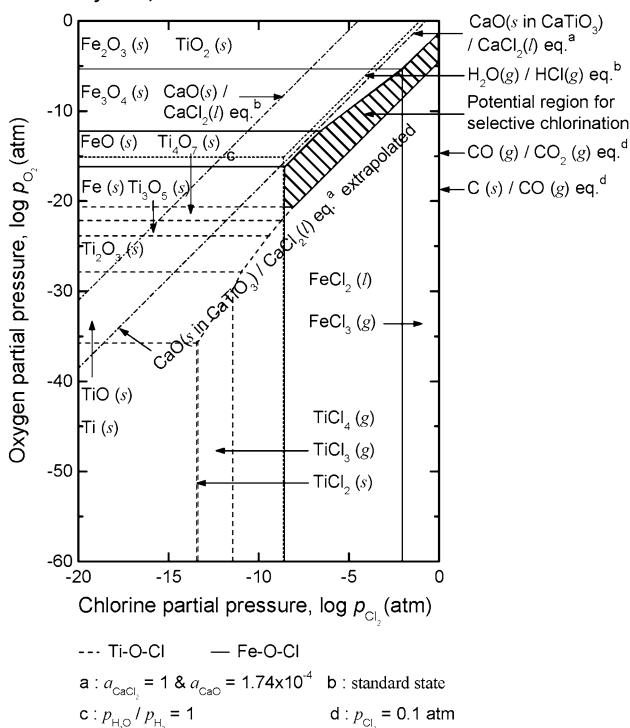
Fig. 5—Combined chemical potential diagram of the Fe-O-Cl (solid line) and the Ti-O-Cl (dotted line) systems at 1240 K (967 °C).
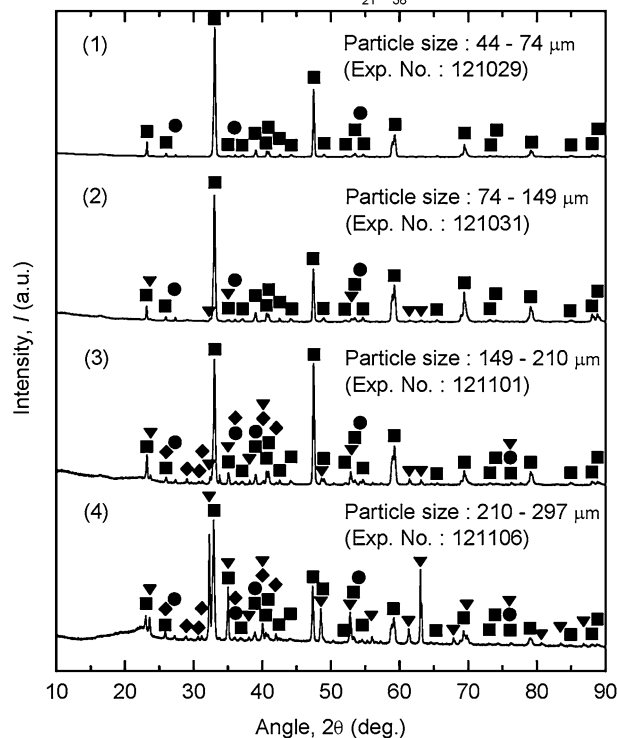

Fig. 6—XRD results of the residues obtained after experiments when Ti ore particles with various ranges of (1) 44 to 74 μm, (2) 74 to 149 μm, (3) 149 to 210 μm, and (4) 210 to 297 μm were used.

$CaTiO_3$, the CaO (s)/CaCl$_2$ (l) eq.[a] line in Figure 5 passes in the vicinity of the potential region for selective chlorination, where FeCl$_2$ is stable. Therefore, the Fe in the Ti ore can be selectively removed as FeCl$_2$, and $CaTiO_3$ can be produced.

In this study, the degree of removal of Fe from Ti ore was evaluated by the Fe removal ratio R_{Fe} introduced by Zheng, detailed in Eq. [5].[13] In addition, the obtained residue was evaluated on the basis of the total mass percent of all elements except Ti and Ca, C_m $(= 100 - (C_{Ti} + C_{Ca}))$, and the results of XRD analysis.

$$R_{Fe}(pct) = 100 \times \left\{ 1 - \left(C_{Fe}^{residue}/C_{Ti}^{residue} \right) / \left(C_{Fe}^{feed}/C_{Ti}^{feed} \right) \right\}$$

[5]

C_{Fe}^{feed} and $C_{Fe}^{residue}$: the mass percent of Fe in the feedstock and residues, respectively,
C_{Ti}^{feed} and $C_{Ti}^{residue}$: the mass percent of Ti in the feedstock and residues, respectively.

A report by Metalysis Ltd, U.K., indicated that rutile (94 to 96 pct TiO$_2$) can be used as a feedstock in the FFC process.[7] Therefore, residues with C_m smaller than 4 to 5 pct, approximately, are appropriate. In this study, a product with C_m smaller than 4 pct is defined as high-grade. Furthermore, the compounds of the residues should be $CaTiO_3$ or/and TiO$_2$.

When the Vietnamese ore with particles smaller than 44 μm was reacted with CaCl$_2$ at 1100 K, 1200 K, and 1240 K (827 °C, 927 °C, and 967 °C) for 10 hours, the mass percent of Fe in the ore decreased from 49.7 to
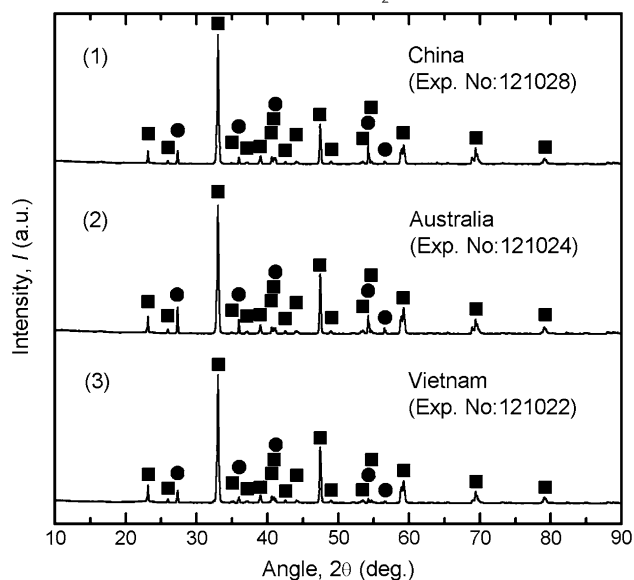

Fig. 7—XRD results of the residues obtained after experiments when various types of Ti ores were used as feedstock: (1) natural Chinese ilmenite, (2) natural Australian ilmenite, and (3) natural Vietnamese ilmenite.
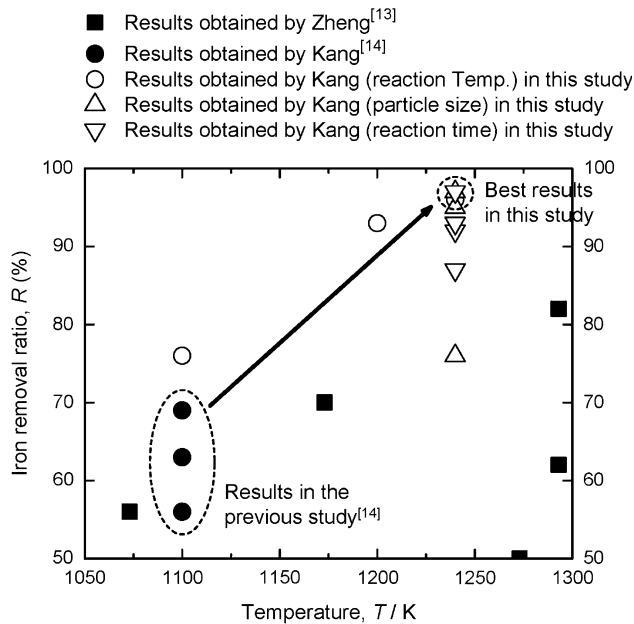
Fig. 8—Comparison of the iron removal ratio obtained by Zheng,[13] Kang,[14] and in this study.

14.2, 4.16, and 2.49 pct, respectively. These results show that as the reaction temperature increased, more Fe in the Ti ore was selectively removed. The reaction rate was increased probably with increasing reaction temperature. In addition, R_{Fe} increased to 96 pct and C_m decreased to 3.43 pct at 1240 K (967 °C), because almost all Fe in the ore was selectively removed by $CaCl_2$.

Table I also shows the influence of the reaction time on the amount of Fe removed from the ore by selective chlorination. When selective chlorination of the Vietnamese ore with particles smaller than 44 μm was carried out at 1240 K (967 °C) for 8, 6, 4, and 2 hours, the mass percent of Fe in the ore decreased from 49.7 to 1.87, 4.90, 4.13, and 8.25 pct, respectively. Experimental results showed the tendency of a greater amount of Fe being removed from the ore with increasing time until reaction times ranging from 8 to 10 hours. In addition, these results showed that reaction times longer than 8 hours are required to increase R_{Fe} above 96 pct and to decrease C_m to below 2.32 pct at most.

When selective chlorination of the Vietnamese ore with particle sizes in the ranges of under 44, 44 to 74, 74 to 149, 149 to 210, and 210 to 297 μm was conducted at 1240 K (967 °C) for 10 hours, the mass percent of Fe in the ore decreased from 49.7 to 2.49, 1.79, 3.07, 14.4, and 29.6 pct, respectively. As shown in the results, the mass percent of Fe was slightly increased from 1.79 to 2.49 pct when the ore with particle size below 44 μm was used. However, these results showed the tendency that as the particle size of the Ti ore increased, smaller amounts of Fe were selectively removed from the ore. In addition, the results showed that the R_{Fe} increased to 97 pct and C_m decreased to 2.41 pct at most, when the particle size of the ore is smaller than 74 μm.

The selective chlorination of Fe in the ore by $CaCl_2$ proceeds from the outside to inside. During the chlorination reaction, $CaTiO_3$ layer is generated to cause a diffusion-controlled process as in the shrinking core model.[20] When the $CaTiO_3$ layer blocks the reaction between Fe in the ore and $CaCl_2$, the removal of Fe significantly decreases. The effect of the diffusional barrier on the conversion is decreased with decreasing particle size. This implies that the larger the particle size, the more unreacted the core remains under identical conditions when the particle size is large enough to incomplete removal of Fe.

Figure 6 shows the XRD analysis results of residues from Ti ore with various particle sizes. As shown in Figures 6 and 7 (3), when the size of the ore particles was smaller than 74 μm, $CaTiO_3$ and TiO_2 were the main products. However, when the particle size was larger than 74 μm, $FeTiO_3$ was also identified among the products. This can be understood based on the previous discussion[14]: with the ore particles in the 74 to 297 μm range, 3.07 to 29.6 pct of the Fe remained in the residues because chlorination of Fe by $CaCl_2$ did not proceed in the center parts of the ore particles, owing to the formation of $CaTiO_3$.

In addition, peaks corresponding to $CaTi_{21}O_{38}$ were also identified in Figure 6 depending on the samples, although the intensity of the peaks of the compound was weak. The main compounds of the Ti ores used are $FeTiO_3$ and TiO_2, as shown in Reference 15. However, small amounts of titanium sub-oxides (TiO_n) including magneli phases (Ti_nO_{2n-1}, $4 \leq n \leq 9$)[21] may exist in the ores. As a result, $CaTi_{21}O_{38}$ may form by the reaction between the titanium sub-oxides with CaO. However, the exact reason for the formation of $CaTi_{21}O_{38}$ is still under investigation. The formation of $CaTi_{21}O_{38}$ also affects the activity of CaO. However, as shown in Figures 6 and 7, $CaTiO_3$ is the main compound in the residues. Therefore, in this study, only the influence of the formation of $CaTiO_3$ on the activity of CaO was discussed.

The investigation of the influence of reaction temperature, reaction time, and particle size of the ore on selective chlorination showed that the reaction temperature should be above 1240 K (967 °C), the reaction time should be longer than 8 hours, and the particle size of the ore should be less than 74 μm. Under these conditions, R_{Fe} increased to 96 to 97 pct and C_m decreased to 2.32 to 3.49 pct. On the basis of these results, when selective chlorination was conducted at 1240 K (967 °C) for 10 hours using the Australian and Chinese ores with particle sizes below 44 μm as feedstock, the mass percent of Fe in the ores decreased from 46.7 to 1.59 pct and from 45.4 to 1.35 pct, respectively. Figure 7 shows that $CaTiO_3$ and TiO_2 were mainly obtained after experiments. It can thus be concluded that selective chlorination using $CaCl_2$ for the production of high-grade $CaTiO_3$ can proceed using various types of Ti ores as feedstock.

Regarding the removal of impurities in the Ti ore, the experimental results showed that selective chlorination also reduced the mass percent of Mn in the ores. As shown in Table I, when the Vietnamese, Australian, and Chinese ores were used, the mass percent of Mn decreased from 3.47 to 0.13 pct, from 1.69 to 0.06 pct, and from 2.79 to 0.11 pct, respectively. It is expected

Table II. Comparison of the Results of the Selective Removal of Iron From Ti Ore obtained in This Study and Those Obtained by Zheng[13] and Kang et al.[14,22]

List	Kang et al. (this study)	Kang et al.[14]	Kang et al.[22]	Zheng[13]
Source country of feedstock (ilmenite)	Vietnam, Australia, China	Vietnam, Australia, China	Vietnam, Australia, China	Vietnam
Mass percent of iron of the Vietnamese feedstock (mass pct)	49.7	49.7	49.7	51.3
Mass percent of iron after the selective chlorination (mass pct)	2.22	0.27	1.24	16.7
Furnace type	vertical	horizontal	horizontal	vertical
Heating method	electric resistance	electric resistance	electric resistance	R.F. induction
Atmosphere (H_2O bath Temp.)	Ar flow	vacuum	Ar + H_2O (303 K/30 °C) flow	N_2 + H_2O (298 K/25 °C) flow
Chlorinating agent	$CaCl_2$	HCl from $CaCl_2$	HCl from $MgCl_2$	$CaCl_2$
Crucible	Mo-lined nickel	Mo-lined quartz	Mo-lined quartz	Ni-lined carbon
Reaction temperature, T/K ($T'/°C$)	1240 (967)	1100 (827)	1000 (727)	1293 (1020)
Reaction time, t_r'/h	20	5	7	12
Weight of Ti ore used, w_{ore}/g	3	0.1	0.1	4
Weight of MCl_2 used*, w_{MCl2}/g	30	3	3	2
Particle size of Ti ore, $d_{ore}/\mu m$	Under 44	44-74	44-74	No information
Product after experiment	$CaTiO_3$	TiO_2	TiO_2	$CaTiO_3$
Mechanism claimed	$TiO_2/CaCl_2/CaTiO_3$ eq.	HCl/H_2O eq. under $TiO_2/CaCl_2/CaTiO_3$ eq.	HCl/H_2O eq. under MgO/$MgCl_2$ eq.	$TiO_2/CaCl_2/CaTiO_3$ eq. or HCl/H_2O eq. under $TiO_2/CaCl_2/CaTiO_3$ eq.

* M = Ca or Mg.

that the Mn was removed through the reaction in Eq. [6].[18] The standard Gibbs energy of the reaction shown in Eq. [6] has a large positive value. Despite this, the reaction can proceed, because the activity of CaO is lowered to 1.74×10^{-4} at 1240 K (967 °C) when the formation of $CaTiO_3$ is taken into consideration.[18]

$$MnO(s) + CaCl_2(l) = MnCl_2(l) + CaO(s) \quad [6]$$

$$\Delta G_r^\circ = 65.5 \text{ kJ at } 1240 \text{ K} (967 °C)$$

$$\Delta G_r = -23.8 \text{ kJ at } 1240 \text{ K} (967 °C)$$
$$\text{when } a_{CaO} = 1.74 \times 10^{-4}$$

In order to check the feasibility of scale-up of the selective chlorination using $CaCl_2$ for the production of $CaTiO_3$, the mass change of feedstock was measured. The weight of the Ti ore used was increased from 0.5 to 3.0 g, where ore with particle size below 44 μm was used for the reaction carried out at 1240 K (967 °C) for 20 hours. Consequently, the mass percent of Fe decreased from 49.7 to 2.22 pct owing to the selective removal of Fe, as shown in Table I. In addition, the results of XRF analysis showed that Mn was also removed by the selective chlorination: the mass percent of Mn decreased from 3.47 to 0.25 pct. These results show that selective chlorination using $CaCl_2$ for the production of $CaTiO_3$ can be scaled up. However, because the upgrading of 3.0 g of Ti ore required 20 hours, further research on the scaling up would be required to improve the efficiency of the process.

The maximum R_{Fe} calculated from the results reported in the previous study[14] was 56 to 69 pct when the Vietnamese, Australian, or Chinese ore with particle sizes in the range of 74 to 149 μm was reacted with $CaCl_2$ at 1100 K (827 °C) for 5 hours, as shown using solid black circles in Figure 8. A possible explanation for R_{Fe} and C_m not reaching 96 to 98 and 4 to 5 pct, respectively, is that the particle size was not smaller than 74 μm, the reaction temperature was not higher than 1240 K (967 °C), and the reaction time was not longer than 8 hours. In addition, the maximum R_{Fe} reported by Zheng was 82 pct when the Vietnamese ore (4.0 g) was reacted with $CaCl_2$ (2.0 g) at 1293 K (1020 °C) for 12 hours. The present results show that low R_{Fe} was achieved because pulverization of the ore was not enough to make the particles smaller than 74 μm and/ or the reaction time for chlorination of 4.0 g of the ore was not enough. It is evident from these results that sufficient Fe removal is difficult to achieve when the reaction temperature, particle size, and reaction time are not optimized.

Table II compares the results of the selective removal of Fe from Ti ore obtained in this paper with those obtained by Zheng[13] and Kang et al.[14,22] As shown in Table II, one of the important findings of this study is that it demonstrated the feasibility of the scale-up of selective chlorination using $CaCl_2$ for the production of high-grade $CaTiO_3$. In addition, a Fe removal ratio of 96 to 98 pct was achieved in this study, significantly higher than the 82 pct ratio obtained by Zheng.[13]

IV. CONCLUSIONS

An effective selective chlorination process using $CaCl_2$ as a chlorinating agent for upgrading Ti ore was investigated for the production of high-grade $CaTiO_3$. After assessing the effects of various experimental parameters on the selective chlorination, an experiment was conducted to evaluate the scaling-up feasibility of the selective chlorination process. Experimental results showed that Fe was selectively and directly removed as $FeCl_2$ (l, g) from the various types of Ti ores studied, and that $CaTiO_3$ was produced in a single step. The experimental results also showed that the amount of Fe removed from the Ti ore increased with increasing reaction temperature and time, as well as with decreasing particle size of the Ti ore.

When selective chlorination was conducted using Vietnamese ore particles of size below 74 μm at 1240 K (967 °C) for more than 8 hours, the mass percent of Fe in the Ti ore decreased from about 50 to 1.8 pct by XRF analysis. In addition, the mass percent of Fe in the Australian and Chinese Ti ores decreased from 47 to 1.6 pct and from 45 to 1.4 pct by XRF analysis, respectively, when the experiments were conducted at 1240 K (967 °C) for 10 hours and with particles smaller than 44 μm. Furthermore, the experiments demonstrated the scaling-up feasibility of the selective chlorination process using $CaCl_2$, a process that can therefore be applied for the production of high-grade $CaTiO_3$.

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