

Novel Synthesis of High Pure Titanium Trichloride in Molten CaCl_2

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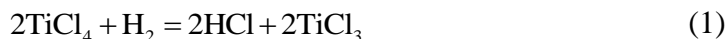
A novel synthesis and enrichment processes for high pure TiCl_3 in molten CaCl_2 were experimentally investigated in this study. Two steps were carried out: the first is the preparation of titanium subchloride, and the second is the enrichment process of TiCl_3 with HCl gas. The titanium subchloride was prepared by the reaction of titanium tetrachloride with metallic titanium in molten CaCl_2 . The HCl gas was used to purify the melt before a series of experiments were done. Also, it was introduced into the melt when TiCl_2 reached to the saturated solubility (7.89 wt.%) at 1123 K. The power of high pure TiCl_3 was collected on the top container of special designed equipment. The collection efficiency of TiCl_3 keeps above on 95%, and the utilized efficiency of HCl decreased with the intruding rate increasing. X-ray diffraction and EDS results demonstrated that the products were pure TiCl_3 . SEM result disclosed that the pure TiCl_3 was dense and homogeneous with an agglomerative structure.

Keywords: Ytria-stabilized zirconia electrode; Subchloride titanium; Pure TiCl_3 ; HCl gas; CaCl_2 melt;

1. INTRODUCTION

The electrochemistry and thermodynamic properties of titanium subchlorides in molten salts has been the subject of many investigations [1-5]. It was disclosed that titanium ions are present in the electrolyte in different valences may favor reoxidation and disproportionation reactions [6-9]. They will result in a very low current density and complication for the electrodeposition process [10-11]. Therefore, it is meaningful for the foundation studies of the titanium subchloride (TiCl_x , $x=2, 3$) which have been used as a titanium ions source material in molten salt for the recovery of metallic titanium by chloride metallurgy [12-16], electrolysis [17-18] and disproportionation [6, 7, 16].

The synthetic process for obtaining titanium subchlorides mixture by the reaction of titanium tetrachloride with metallic titanium at 1273 K was investigated [16]. However, a very small number of studies were conducted on high pure titanium trichloride (TiCl_3) synthesis that was employed in molten salt media directly. Thus far, TiCl_3 has been prepared by reducing TiCl_4 with hydrogen gas (H_2) in Re. (1) at high temperatures [19-20], or by the aluminothermic reduction of TiCl_4 or distillation [21].



However, the approximate volatility and tendency to disproportionation of TiCl_3 make the clean separation of TiCl_3 from other metal chlorides difficult. Furthermore, it is hard to occur for the Re. (1) by calculated the Gibbs free energy (83.73 kJ/mol) at 1123K.

A new synthetic and enrichment processes for high pure TiCl_3 in the molten salt were experimentally investigated in this study. A simple and compact reaction apparatus was used which is suitable for the reaction of TiCl_4 with metallic titanium producing titanium subchloride. Based on this background, experiments for the enrichment process of TiCl_3 in molten salt were carried out.

2. EXPERIMENT

2.1 TiCl_x synthesis in molten salt

The calcium chloride is expected to work as a medium for its low vapour pressures. The vapour pressures of the different molten salts at the respective likely minimum operating temperatures are given in Table 1 [22].

Table 1. Salt vapor pressures of chloride in molten at different temperatures.

Salt [22]	M.P. T / K	$P_{\text{vap}} / \text{Pa}$
LiCl	903	4.2
NaCl	1094	60
MgCl ₂	1007	61
CaCl ₂	1135	0.2

As can be seen, CaCl_2 has by far the lowest vapour pressure. Anhydrous CaCl_2 (Sinopharm Chemical Reagent Co., Ltd. analytical grade $\geq 99.99\%$, 100 g) was dried under vacuum for more than 24 hours in a alumina crucible (95 mm outer diameter, 120 mm height, 5 mm thickness) and heated to 1123 K in an electric furnace with high pure argon gas (Sinopharm Chemical Reagent Co., Ltd. analytical grade $\geq 99.999\%$) atmosphere. Hydrogen chloride gas (HCl , Sinopharm Chemical Reagent Co., Ltd. analytical grade $\geq 99.99\%$) was bubbled through the melts to remove O^{2-} dissolved in the molten salt. Then, high pure argon gas was introduced into the fused salt to remove excess HCl gas.

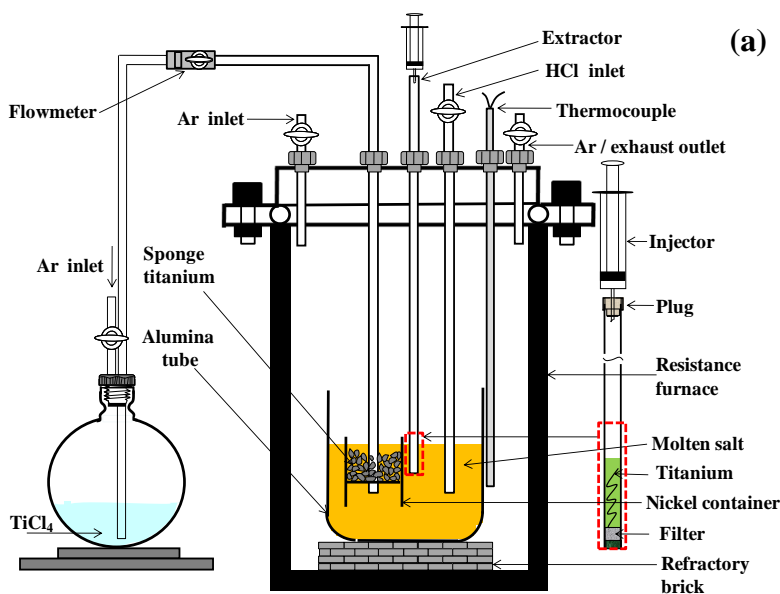
The concentration of O^{2-} in the molten salt was determined by *emf* method with the yttria-stabilized zirconia electrode (YSZE). The oxide concentration indicator electrode consisted of a tube of YSZE (3 mm diameter). The reference electrode was an Ag/AgCl electrode, which consisting of a silver wire (0.5 mm diameter) contained in a mulite tube, and dipped into a silver chloride solution (4 wt.%) in the CaCl_2 . The auxiliary electrode was a graphite rod (6 mm diameter). The electrodes active

surface area were determined by the depth of immersion and corrected for the height of the meniscus. The variation of the YSZE potential was performed with *emf* method using a PARSTAT 4000 potentiostat (Princeton Applied Research, USA) controlled by a personal computer and specific software (VersaStudio, PAR, USA). The Nernstian behaviour of the system was demonstrated by measuring the change in electrode potential as purification with HCl gas [23-24]. The relationship between concentration of oxide and potential can be expressed as Eq. (2):

$$E_{\text{O}_2/\text{O}^{2-}} = E_{\text{O}_2/\text{O}^{2-}}^* - \frac{RT}{2F} P_{\text{O}_2} \quad (2)$$

where $E_{\text{O}_2/\text{O}^{2-}}$ is the equilibrium potential of O_2/O^{2-} system (in V); $E_{\text{O}_2/\text{O}^{2-}}^*$ is an apparent standard potential of the system (in V) and P_{O_2} is $\ln x_{\text{O}_2}$.

After purification, titanium powders (Sinopharm Chemical Reagent Co., Ltd. analytical grade 99.99%) that used as the feed materials in the synthesis experiments were placed in a molybdenum basket [25] (Mo, 99%, octagonal pillar shape, 45 mm outer diameter, 100 mm height, 5 mm thickness) immersing in molten CaCl_2 . Titanium tetrachloride is readily available commercially at pure of 99.9%, and it was purified by fractional distillation in this experiment. The schematic illustration of the experimental apparatus for the TiCl_x ($x=1, 2$) synthesis by the reaction of TiCl_4 with metallic titanium is shown in Fig. 1(a). Liquid TiCl_4 was fed into this reaction container at the rate of 0.13~0.72 g/min by dropping it from the top of the chamber through quartz feed tube. It was expected that the TiCl_4 was supplied in the form of gas bubble at elevated temperatures reacted with titanium powder in the molten CaCl_2 . After experiment, the molybdenum basket with titanium powder was removed from the molten salt. The molten salt in the alumina crucible and the residual titanium in the basket were gradually cooled in the furnace and recovered in the argon atmosphere at room temperature.



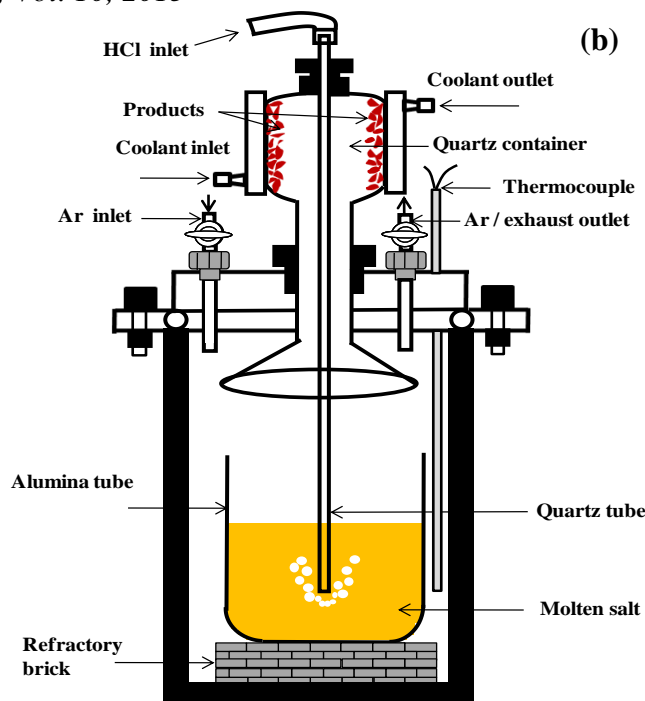


Figure 1. (a) Schematic illustration of an experimental apparatus for TiCl_x synthesis by the reaction of TiCl_4 with metallic titanium; (b) Schematic illustration of an experimental apparatus for enrichment of TiCl_3 .

2.2 Enrichment of TiCl_3

A schematic illustration of the experimental apparatus for TiCl_3 enrichment in molten CaCl_2 is shown in Fig. 1(b). The CaCl_2 - TiCl_x salt (TiCl_2 concentration of 7.89 mass%, 100g) that was obtained from the TiCl_x synthesis process was filled into an alumina crucible, and it was heated to 1123 K. Then, the HCl gas was introduced into molten CaCl_2 with different rates afterwards. It was confirmed by Sekimoto [21] that the vapor pressure of TiCl_3 is so different from other chlorides that pure TiCl_3 can be obtained by evaporation.

After reactions, the samples obtained from quartz container were cooled to room temperature under argon gas atmosphere then covered with a polyimide film to prevent the samples from reacting with the moisture. The samples were transferred to the glove box where the content of water and oxygen was maintained under 0.2 ppm.

2.3 Analysis

The quantitative analysis of different oxidation states of titanium ions consists of three main steps [26-28]. First, the concentration of Ti^{2+} was measured by H_2 volumetric analysis. The method is based on the fact that TiCl_2 can react with hydrochloric acid and generates H_2 gas in hydrochloric acid solution which is expressed by Re. (3):



The oxygen dissolved in diluted hydrochloric acid can oxidize Ti^{2+} in the process of determination of Ti^{2+} , which can cause the underestimation of Ti^{2+} concentration in the sample. Vacuum-deaeration was used to remove the O^{2-} dissolved in deionized water then the deoxygenized water. The deoxygenized hydrochloric acid solution was saturated by bubbling of high pure H_2 to prevent the H_2 generated by Re. (3) dissolving in the hydrochloric acid solution before the reaction. After the reaction, all of the Ti^{3+} in the solution consists of Ti^{3+} which is original in the sample and the Ti^{3+} generated by Re. (3). The concentration of Ti^{3+} in the solution was determined by the titrimetric analysis using $NH_4Fe(SO_4)_2$ aqueous solution which was acidified with sulfuric acid. The Ti^{3+} in the solution reacts with Fe^{3+} as Re. (4):



The titration process was conducted in high pure argon atmosphere. Finally, the total titanium ions (Ti^{2+} , Ti^{3+} and Ti^{4+}) amount in the other solution was determined by diantipyrylmethane spectrophotometry.

The crystal phases and morphology of products were characterized by X-ray diffraction (XRD, Rigaku, D/max-RB) and field emission scanning electron microscopy (FESEM, JEOL, JEM-6701F) operated at an accelerating voltage of 30 kV, together with EDS was used to study the surface morphology and elements content of the samples, respectively.

3. RESULTS AND DISCUSSION

The variation of $P_{O^{2-}}$ during the purification of the melt with HCl is disclosed by YSZE shown in Fig. 2.

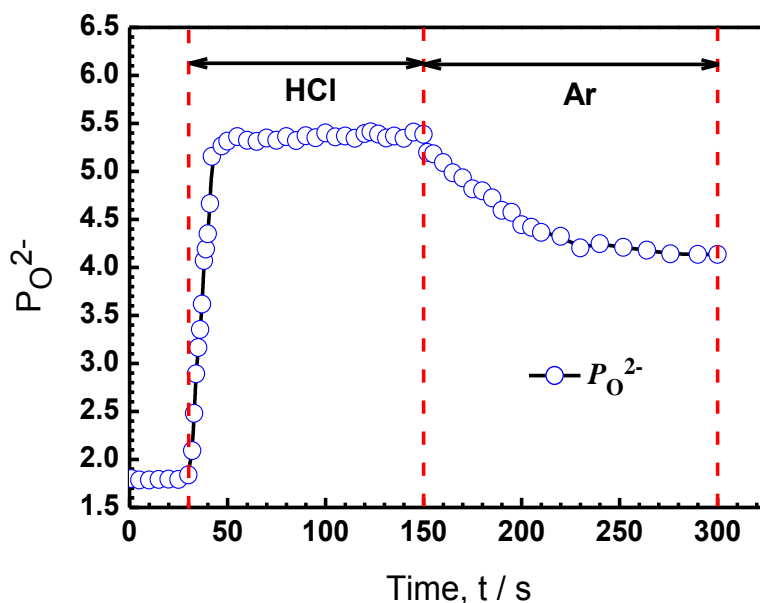


Figure 2. Variation of the $P_{O^{2-}}$ during the purification of the melt by HCl gas which measured with an oxide specific electrode based on YSZE.

One can see from Fig. 2 that the residual concentration of O^{2-} ions in the melt after fusion under vacuum is about $1.0 \times 10^{-1.78}$ mol/kg (265 ppm). When the HCl gas was passed through the salt, there

was a rapid decrease in the oxide-ion concentration which maintained a near constant value of $1.0 \times 10^{-5.41}$ (0.06 ppm). However, there was a rapid increase in oxide concentration as soon as argon was bubbled through the melt, which nearly reached to $1.0 \times 10^{-4.13}$ mol/kg⁻¹ (1.18 ppm) in the melt. It was owned to the traces of water contained in the argon gas, and reacting with the salt according to [23]:



So the residual oxide concentration is conditioned by the quality of the argon employed, a similar behavior observed in other molten chlorides.

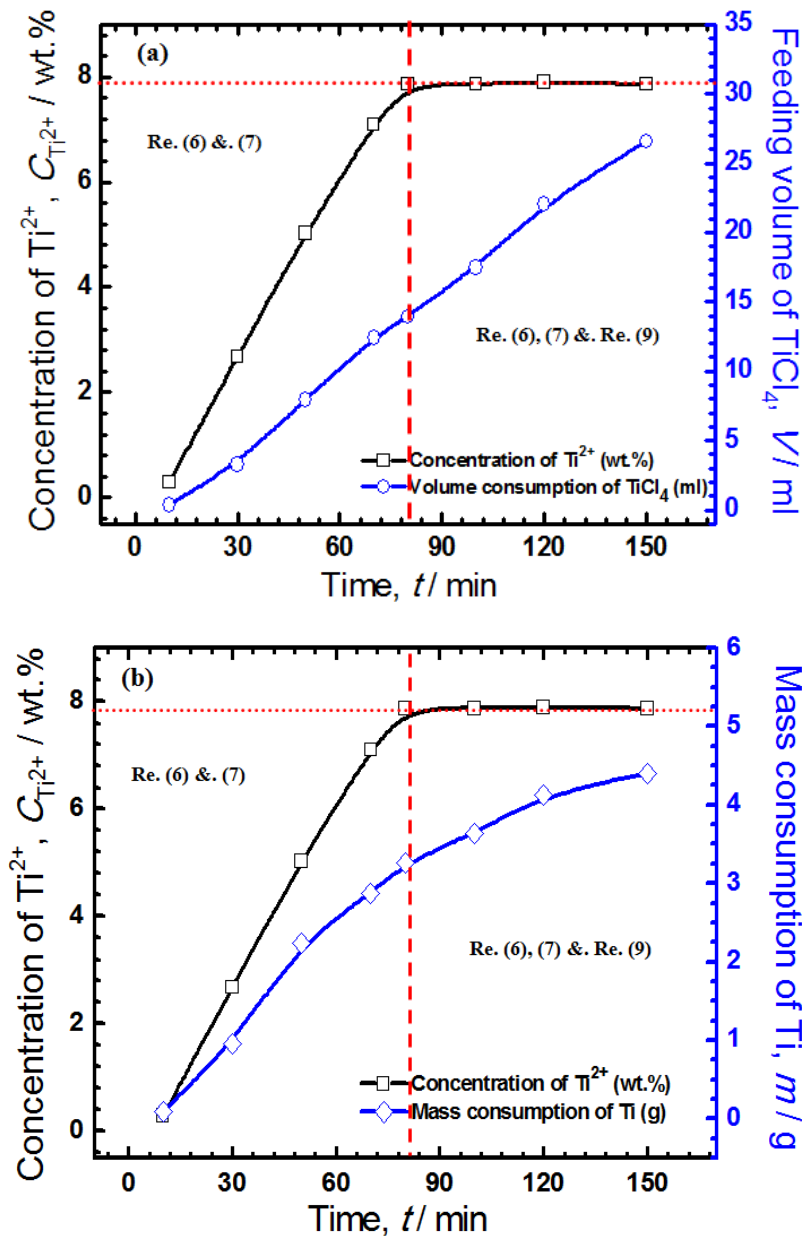


Figure 3. Various concentration of Ti^{2+} with the relationship of (a) The feeding volume of TiCl_4 ; (b) mass consumption of metallic titanium.

Fig. 3(a) shows the analytical concentrations of Ti^{2+} various in molten $CaCl_2$ while feeding of $TiCl_4$. It increases sharply and the consumption of titanium has the same tendency while introducing $TiCl_4$ in Fig. 3(b). The mainly reactions accord to Re. (6) and Re. (7):



The Gibbs free energies of formation (ΔG_f^0) of $TiCl_2$ and $TiCl_3$ are -5.362 kJ/mol and -2.035 kJ/mol, respectively. Therefore, besides the $TiCl_2$, the $TiCl_3$ will be obtained at the same time.

Table 2. The total yield mass of $TiCl_3$, the mass in the melt and the collected from the top of container.

Exp. No.	Total Ti content, wt.%	Concentration of Ti^{2+} ion, $x_{Ti^{2+}}$ / mol%	Concentration of Ti^{3+} ion, $x_{Ti^{3+}}$ / mol%	Equilibrium Constant, K_c	Std.
A	6.01	0.0772	0.0064	0.089	
B	5.20	0.0670	0.0054	0.097	
C	4.54	0.0588	0.0043	0.092	0.0059
D	4.34	0.0561	0.0043	0.104	
E	4.20	0.0544	0.0040	0.099	

Where $x_{Ti^{2+}}, x_{Ti^{3+}}$ is the molar fraction of Ti^{2+} and Ti^{3+} , and K_c is expressed as $K_c = x_{Ti^{3+}}^2 \cdot x_{Ti} / x_{Ti^{2+}}^3$.

Actually, the titanium trichloride that was detected comes from two sources: one is the products from Re.(7), and the other yields from the disproportionation among metallic titanium, $TiCl_2$ and $TiCl_3$ ($3TiCl_2 = Ti + 2TiCl_3$). Table 2 shows the equilibrium constant ($K_c = x_{Ti^{3+}}^2 \cdot x_{Ti} / x_{Ti^{2+}}^3$) for the disproportionation. The average value of K_c is 0.096 (with Std. of 0.059) at 1123K in molten $CaCl_2$.

Table 3. Chemical analysis results of $x_{Ti^{2+}}, x_{Ti^{3+}}$, and K_c with filtering.

Time, t / s	$TiCl_3$ in the melt, m_{liquid} / g	Collection of $TiCl_3$, m_{solid} / g	Yield of $TiCl_3$, m_{yield} / g
30	0.548	0.157	0.705
50	1.367	0.632	1.999
70	2.322	0.973	3.295
90	2.757	1.201	3.958

The yield of $TiCl_3$ can be expressed by Eq. (8) and results list in Table 3.

$$m_{yield} = m_{liquid} + m_{solid} \tag{8}$$

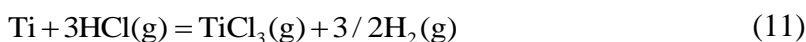
Where m_{yield} is the total mass of $TiCl_3$, m_{liquid} is the mass of $TiCl_3$ in molten $CaCl_2$, m_{solid} is the collection mass of $TiCl_3$ on the top of container show in Fig 1(b).

The results of first column in Table 3 show analytical concentration of $TiCl_3$, and they are corresponding with the analytical concentration of $TiCl_2$ according to above disproportionation when containing metallic in the melt. The solid state $TiCl_3$ was observed on the top container. It was indicated that one part of $TiCl_3$ can be volatilized from the melt for its vapor pressure is different from other chlorides. Results show in the second column of Table 3.

Moreover, Fig. 3(a) and Fig. 3(b) show the concentration of Ti^{2+} keeps to a constant as 7.89 wt.% while $TiCl_4$ and metallic titanium were consumed in molten $CaCl_2$. The conclusion can be made that the saturated solubility of $TiCl_2$ in $CaCl_2$ at 1123K is 7.89 wt.%. Therefore, the reactions occurring at this time are Re. (6), (7) and (9). The production of $TiCl_2$ and its consumption reach to an equilibrium status.



The HCl gas was introduced into $CaCl_2$ melt that contained $TiCl_2$ with the concentration of 7.89 wt.%. The predominant reactions happened are expressed as Re. (10) and Re. (11):



The Gibbs free energies of formation of $TiCl_3$ are -11.10 kJ/mol and -42.93 kJ/mol, respectively.

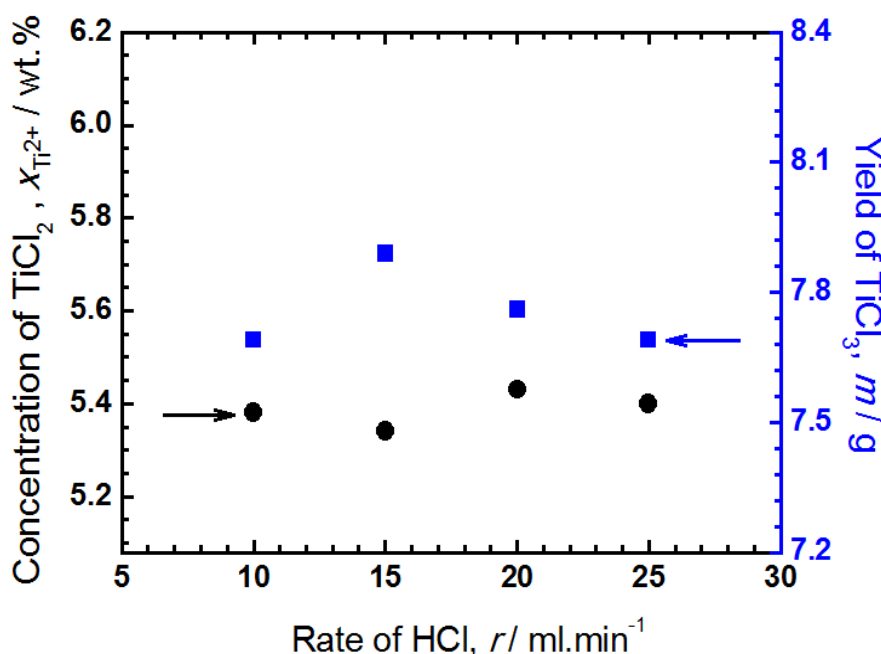


Figure 4. The relationship between concentration of $TiCl_2$ and yield of $TiCl_3$ at different introducing rate of HCl gas.

Fig. 4 shows the relationship between concentration of $TiCl_2$ and yield of $TiCl_3$ at different introduction rate of HCl gas. The concentration of $TiCl_2$ decreased while introducing of HCl gas. The

collection efficiency of $TiCl_3$ is calculated as Eq.(12). Also, the utilized efficiency of HCl is calculated as Eq.(13).

$$\eta = m_{\text{yield}} / m_{\text{theory}} \times 100\% \tag{12}$$

$$\eta' = m'_{\text{yield}} / m'_{\text{theory}} \times 100\% \tag{13}$$

Where m_{theory} is the mass of $TiCl_3$ calculated with consumed $TiCl_2$ in theory, and m'_{theory} is the mass of $TiCl_3$ for consumed HCl gas in theory.

Table 4. Collection efficiency of $TiCl_3$, utilized efficiency of HCl under different introducing rate of HCl gas.

Rate of HCl, $R / \text{ml min}^{-1}$	Yield of $TiCl_3$, $m_{\text{yield}} / \text{g}$	Theory yield of $TiCl_3$, $m_{\text{theory}} / \text{g}$	Collection efficiency of $TiCl_3$, $\eta / \%$	Efficiency of HCl, $\eta' / \%$
5	7.69	8.09	95.10	78.30
10	7.99	8.22	97.20	50.10
15	7.76	7.93	97.80	38.50
20	7.69	8.03	95.70	31.20

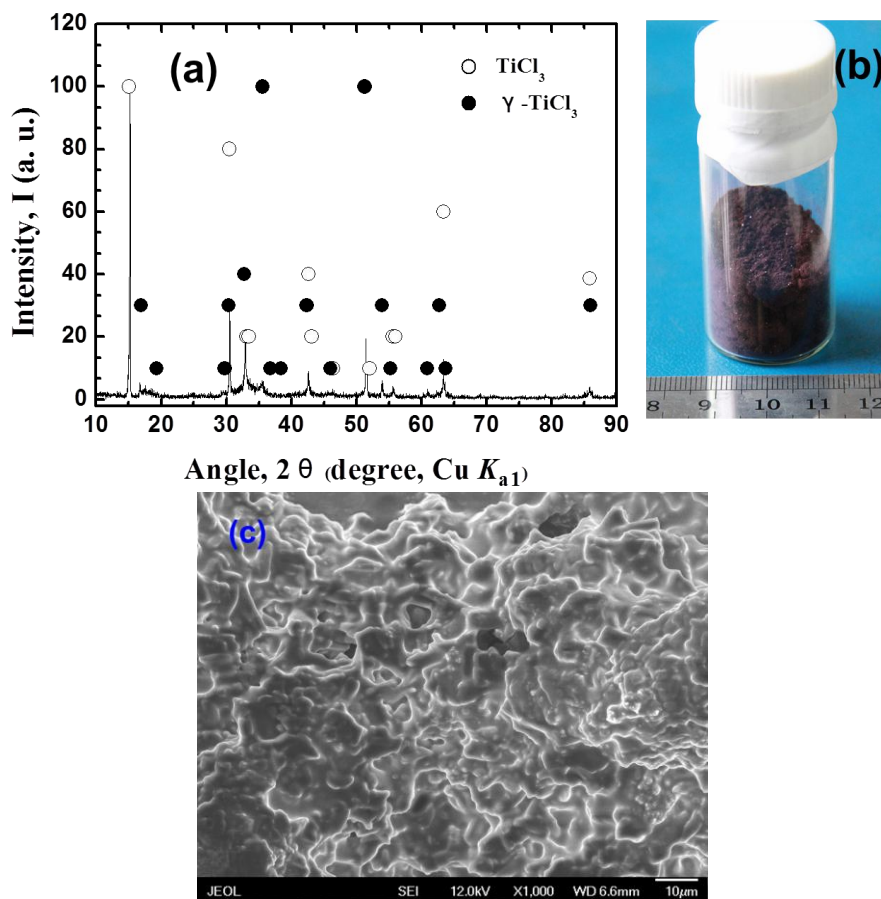


Figure 5. (a) X-ray diffraction pattern, (b) photo and (c) SEM micrograph of $TiCl_3$.

The results show in Table 4. With the increasing of the introducing rate of HCl gas, the collection efficiency of $TiCl_3$ keeps above on 95%, and the yield of $TiCl_3$ is in accordance with the decreasing of $TiCl_2$. However, the utilized efficiency of HCl gas decreased when increases the introducing rate. Therefore, the rate controlling step for the reaction of $TiCl_2$ with HCl gas is not the introducing rate of the HCl gas. The HCl will effuse as tail gas if the introducing volume higher than 20 ml/min in the experiments.

The sample and the X-ray diffraction analysis results show in Fig. 5. Fig. 5(b) shows that the fine power products with color of purple. The composition was identified by X-ray diffraction analysis which is $TiCl_3$ and $\gamma-TiCl_3$ (gamma structures). The micrograph of the product was confirmed by the SEM characterization show in Fig. 5 (c). It can be seen that the phase is dense and homogeneous with an agglomerative structure.

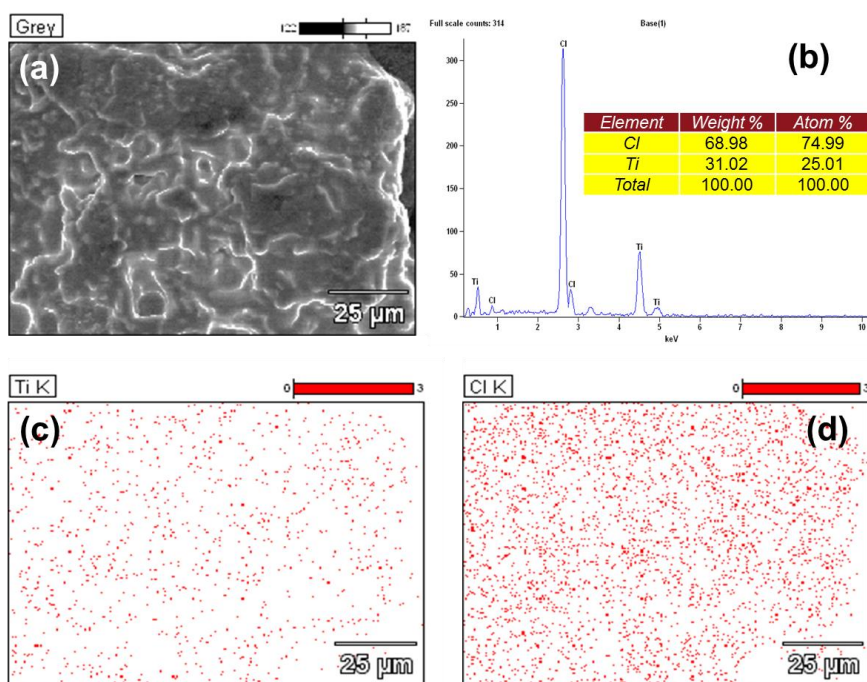


Figure 6. (a) EDS survey spectra at the surface, (b) EDS characteristic spectra, (c) EDS of elements mapping for Ti, (d) EDS of elements mapping for Cl.

Fig. 6 shows the EDS survey spectra result at the surface. The characteristic spectra show that there are two elements (Ti and Cl) for the selected surface in Fig. (b). The EDS of elements mapping for Ti and Cl show in Fig. 6(c) and (d) after surface scanned. The EDS results show that the distributions are uniform for the two elements which are consistent with the results shown in SEM. The elements content can be read in Fig. 6(b). The atom ratio of chloride and titanium, n_{Cl}/n_{Ti} , is 2.998 which mean the sample is $TiCl_3$. It is very close to the results discussed by Sekimoto [21]. In their work, the $TiCl_3$ was prepared by distillation. The cationic concentration of aluminum was low and the molar ratio of Cl and Ti was calculated to be 3.01. However, the elements of Fe, Cr and Ni other than

Ti and Al were detected in the samples. The impurity elements in the detective scope were not found in the samples for the quartz container was used in our experiments.

In summary, the synthesis process of high pure TiCl_3 in molten CaCl_2 can be concluded in two steps. The first step is that synthesis of titanium subchloride mixtures by the reaction TiCl_4 with Ti. The TiCl_3 will be collected when TiCl_4 was enough. The products are mainly TiCl_2 when titanium is excessed yet. The TiCl_2 was oxidized by HCl gas when it reaches to the saturated solubility in the second step, and TiCl_3 will volatilize on the top collector. The schematic illustration of an expected reaction system for TiCl_3 synthesis is show in Fig. 7. The reaction interface means the physical contact between reagents in molten CaCl_2 .

The novel synthesis of high pure TiCl_3 in molten CaCl_2 is easy to control and operate. Moreover, it is available in mass production and can be used in titanium production in novel process.

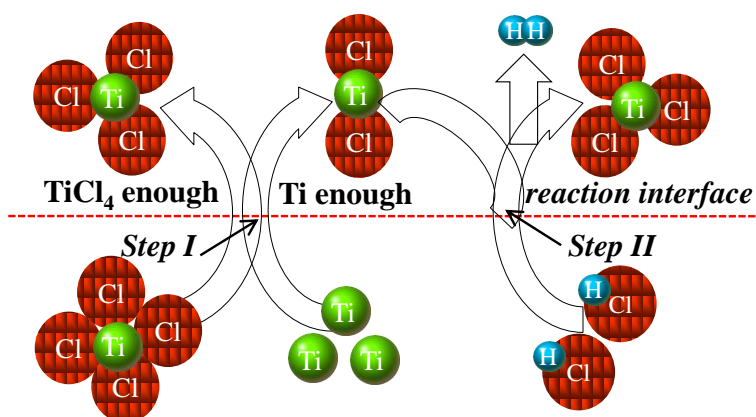


Figure 7. Schematic illustration of an expected reaction system for TiCl_3 synthesis by the reaction of TiCl_4 with metallic titanium in molten CaCl_2 .

4. CONCLUSION

In order to carry out studies on the electrolysis and equilibrium among titanium ions, a novel synthesis and enrichment processes for high pure titanium trichloride (TiCl_3) in molten CaCl_2 were experimentally investigated in this study. The molten salt was purified with HCl gas before experiments were carried out, and then the oxygen content will reduce to 1.18 ppm. There are two steps for synthesis of TiCl_3 : the first is the preparation of titanium subchloride, and the second is the enrichment process of TiCl_3 with HCl gas. The titanium subchloride was prepared by the reaction of titanium tetrachloride with metallic titanium in molten CaCl_2 . The equilibrium constant for the reaction $3\text{TiCl}_2 = \text{Ti} + 2\text{TiCl}_3$ in molten CaCl_2 at 1123K was measured by chemical analysis method in the first step, and the saturated solubility of TiCl_2 in molten CaCl_2 was determined as 7.89 wt.%. The results in the second step disclosed that the collection efficiency of TiCl_3 keeps above on 95%, and the utilized efficiency of HCl gas decreased with the rate increasing in the enrichment step. X-ray diffraction and EDS results demonstrated that the products were pure TiCl_3 . SEM result disclosed that the pure TiCl_3 is dense and homogeneous with an agglomerative structure.

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