Development of Method for Direct Deoxidation of Titanium using Mixtures of Magnesium Chloride and Rare-Earth Chlorides

Takanari Ouchi[1*], Chenyi Zheng[1, 2], Lingxin Kong[1], Toru H. Okabe[1]

1. The Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan
2. Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

t-ouchi@iis.u-tokyo.ac.jp

Abstract

To decrease the cost of Ti sponge, Ti scrap is added during the remelting process to produce an ingot. However, the use of Ti scrap as an additive during this process is limited because Ti scrap is contaminated by oxygen (O) and iron (Fe), which are not removable during the remelting process. Here we introduce a new electrochemical deoxidation process for Ti scrap using a mixture of magnesium chloride ($MgCl_2$) and rare-earth chlorides ($RECl_3$, RE: Y and Ho) as a flux. Ti and carbon were used as the cathode and anode, respectively. Mg is deposited on the Ti cathode and reduces the oxygen in the Ti to oxide ions (O^{2-}). The activity of the generated O^{2-} in the system, $a_{O^{2-}}$, is maintained at a low level through the formation of rare-earth oxychloride (REOCl), and is further decreased by the formation of carbon oxides on the anode. During this process, the concentration of oxygen in the Ti is effectively decreased to 100 mass ppm in the $MgCl_2$-YCl_3 flux at 1,200 K. This new deoxidation method is considered applicable to the recycling process of Ti scrap containing large amounts of oxygen.

1. Introduction

The production of titanium (Ti) scrap is increased along with the demand for Ti products [1-3]. The price of Ti scrap is around one-tenth that of Ti sponge. To decrease the cost of Ti sponge, Ti scrap is thus added during the remelting process to produce an ingot. However, the use of Ti scrap as an additive during the remelting process is limited because Ti scrap is contaminated by oxygen (O) and iron (Fe), which are not removable through the remelting process. Large amounts of scrap are generated during the material flow of Ti, as shown in Fig. 1. Ti scrap with a high O concentration is unsuitable for the remelting process and is thus reused as an additive in the production of steel, aluminum, and other materials or is discarded as waste. To increase the use of Ti scrap as a feed material for producing a Ti ingot, the O concentration of Ti scrap needs to be reduced to less than 500 mass ppm O (equivalent to Ti sponge) in advance through a deoxidation process.
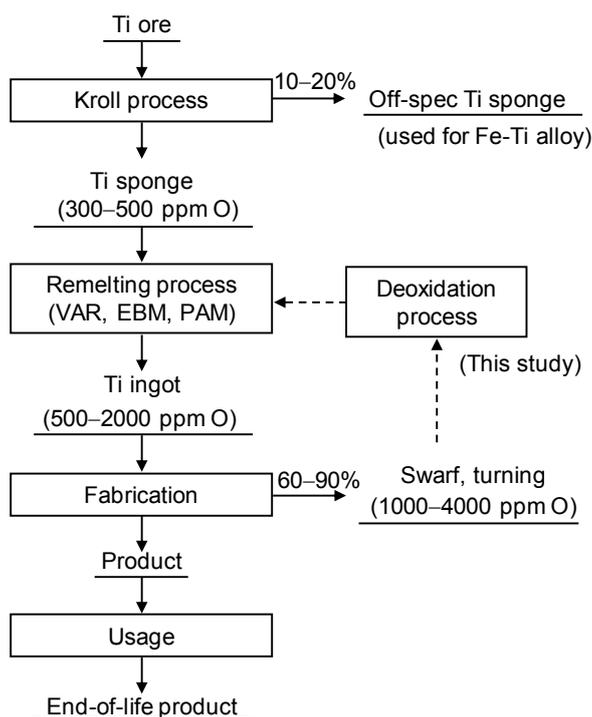

Fig. 1 Material flow of titanium and production of titanium scrap [1-3].

Deoxidation of Ti is extremely difficult owing to the high affinity of Ti for O. Figure 2 shows the oxygen concentration in Ti, $[O]_{Ti}$, in the equilibrium of several metals and their oxides or oxychlorides as a function of temperature calculated using available thermodynamic data [4, 19]. In our recent studies, based on thermodynamic estimations, we proposed that Ti with an extra-low oxygen concentration can be obtained using RE halides as a flux by forming rare-earth oxyhalides (REOXs; X: F, Cl) owing to their high thermodynamic stabilities [8, 9]. For instance, when Ti is deoxidized using yttrium (Y) as the deoxidant in an yttrium chloride (YCl_3) flux, the system is in $Y/YOCl/YCl_3$ equilibrium. The calculated oxygen concentration in Ti in this equilibrium at 1,027 °C (1,300 K) is less than 10 mass ppm O [8]. Only few metals, such as calcium (Ca) and rare-earth metals (REs), have sufficient abilities for the deoxidation of Ti from a thermodynamic perspective. However, if the deoxidation of Ti is feasible using Mg as the deoxidant in a magnesium chloride ($MgCl_2$) flux, the reduction and electrolysis facilities used in the conventional Kroll process can be utilized and are therefore advantageous for practical applications. However, it is impossible to reduce the oxygen content of Ti, $[O]_{Ti}$, to levels of below 1 mass % (10,000 ppm) O simply using Mg and $MgCl_2$ owing to the low deoxidation ability of Mg through the formation of MgO (O $_{in\ Ti}$ + Mg → MgO), as shown in Figure 2. This value cannot be utilized for industrial applications.

To obtain Ti with a low oxygen concentration using Mg as the deoxidant in a $MgCl_2$ flux, the activity of MgO, a_{MgO} (present as oxide ion in the flux, *i.e.*, the activity of oxide ion, $a_{O^{2-}}$), in the system must be reduced to and maintained at a low level during deoxidation. For instance, to obtain Ti with 500 mass ppm

O, a_{MgO} must be decreased to 0.024 at 1,200 K. To decrease the $a_{O^{2-}}$ in molten salt for deoxidation of Ti, an electrochemical method is valid. The oxygen in Ti used as a cathode is reduced by Mg electrochemically deposited on the surface of the Ti and generates O^{2-}. The generated O^{2-} present in the flux is removed from the system as carbon oxide, CO_x (*g*), generated simultaneously on a carbon anode. The oxygen concentration in the Ti sample was decreased to below 200 mass ppm O, and in some cases, below 100 mass ppm O [5, 6]. However, it is not realistic to process large amounts of Ti scrap through this process because a_{MgO} (or $a_{O^{2-}}$) increases during the processing of scraps owing to the small solubility of oxide ions in $MgCl_2$ [7].

To decrease and maintain the activity of MgO, a_{MgO}, to low levels, we developed a new process by adding rare-earth chloride ($RECl_3$) to the $MgCl_2$ flux [3, 8, 9, 11]. In the mixture of $MgCl_2$–$RECl_3$, Mg metal is stable and functions as the deoxidant. Then, O in Ti reacts with Mg and $RECl_3$ to form REOCl through the following reaction:

$$O\ (in\ Ti) + Mg\ (in\ flux) + RECl_3\ (in\ flux) \rightarrow MgCl_2\ (in\ flux) + REOCl\ (s) \qquad (1)$$
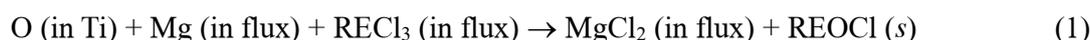
The relationship between the concentration of oxygen in β-Ti ($[O]_{Ti}$ (mass %)) and p_{O_2} can be expressed as follows:

$$1/2\ O_2\ (g) = O\ (1\ mass\ \%,\ in\ \beta\text{-}Ti), \qquad (2)$$

$$\Delta G^{\circ}_{1,Ti} = -2.303 \cdot RT \log \frac{f_O \cdot [O]_{Ti}}{p_{O_2}^{1/2}}, \qquad (3)$$

$$= -583000 + 88.5\ T\ (J) \qquad (4)$$

$$[1,173\text{–}1,373\ K\ (900\text{–}1,100\ °C)]^{[10]}$$

where $[O]_{Ti}$ is the oxygen concentration in Ti expressed relative to 1 mass % (the standard state of oxygen in solid titanium is 1 mass % O). In addition, $\Delta G°_{1,Ti}$ is the standard Gibbs energy of oxygen dissolution in β-Ti, R is the gas constant, *T* is the absolute temperature, and f_O is the Henrian activity coefficient for oxygen dissolved in β-Ti, which is considered to be unity. The oxygen dissolved in Ti is assumed to obey Henry's law.

The deoxidation limit of Ti through the deoxidation reaction in $Mg/MgCl_2/RECl_3/REOCl$ equilibrium can be calculated using Eqs. (5)–(7).

$$O\ (1\ mass\ \%,\ in\ \beta\text{-}Ti) + Mg\ (l) + RECl_3\ (l) = MgCl_2\ (l) + REOCl\ (s) \qquad (5)$$
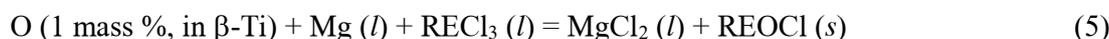
$$\Delta G^{\circ}_{deox,Mg/MgCl_2/REOCl/RECl_3} = -2.303 \cdot RT \log \frac{a_{MgCl_2} \cdot a_{REOCl}}{f_O \cdot [O]_{Ti} \cdot a_{Mg} \cdot a_{RECl_3}}, \qquad (6)$$

$$\Delta G^{\circ}_{deox,Mg/MgCl_2/REOCl/RECl_3} = \Delta G^{\circ}_{f,REOCl(s)} + \Delta G^{\circ}_{f,MgCl_2(l)} - \Delta G^{\circ}_{f,RECl_3(l)} - \Delta G^{\circ}_{1,Ti} \qquad (7)$$

Through this reaction, the process is estimated to reduce the oxygen concentration in Ti to levels dramatically lower than those obtained using the Mg deoxidant in $MgCl_2$, as shown in Fig. 2. We demonstrated that O in Ti, *Co* (mass ppm O), can be decreased through this novel method: For instance, Ti with $2,400 \pm 500$ mass ppm O and $1,600 \pm 300$ mass ppm O were obtained when using $MgCl_2$-10 mol%YCl_3 at 1,300 K and $MgCl_2$-20 mol % $HoCl_3$ at 1,173 K, respectively [3, 11].

To further decrease the $O_{in\ Ti}$ directly from Ti scrap, in more recent studies [12, 16], an electrochemical deoxidation method using Mg as the deoxidant in a mixture of $MgCl_2$ and $RECl_3$ (RE: Y and Ho) was

developed and is introduced in this paper. Furthermore, a new process flow of deoxidation including the electrochemical recovery process for the by-products of the deoxidation reactions, such as $MgCl_2$ and REOCl, is proposed.
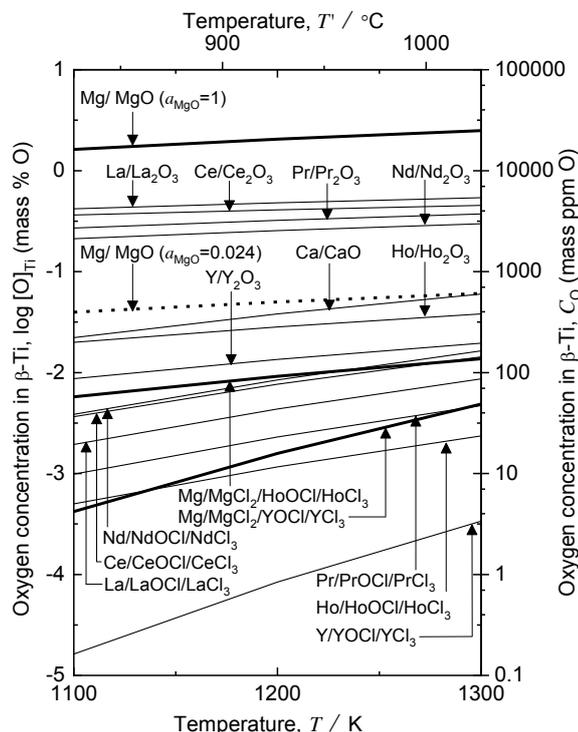

Fig. 2 Temperature dependence of oxygen concentration in β-Ti determined based on M/M_2O_3 and $M/MOCl/MCl_3$ (M: Ho, Y, La, Ce, Pr, or Nd) equilibria; the Mg/MgO, Ca/CaO, $Mg/MgCl_2/YOCl/YCl_3$, and $Mg/MgCl_2/HoOCl/HoCl_3$ equilibria are also shown [4, 8, 11].

2. Material and Experiments

Figure 3 shows a schematic illustration of the experimental apparatus. A Ti wire with a 3 mm diameter and 1100−1200 mass ppm initial O concentration (CP-Ti, Shinkizoku Industries, Co., Ltd.) was used as the sample. The surface area of the Ti wires was 200−300 mm².
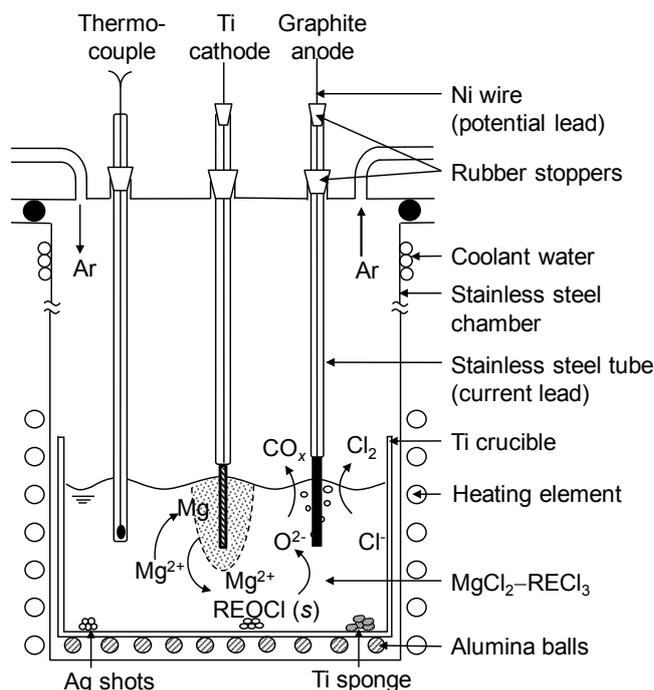

Fig. 3 Schematic of electrochemical deoxidation experiment apparatus.

Approximately 500−1,000 g of anhydrous $MgCl_2$ (≥ 97 %, flake form, Wako Pure Chemical Industries, Ltd.) and approximately 50−100 g metallic Y (≥ 99 %, Santoku Co., Ltd.) or Ho (≥ 99 pct, Santoku Co., Ltd.) was loaded in a Ti crucible (89 mm in diameter, 350 mm in height), and then placed in a stainless-steel chamber. The system was vacuum dried at 673 K (400 °C) for 173 ks (48 h), and the $MgCl_2$ was then melted under an Ar atmosphere at an elevated temperature.

A flux with a composition of $MgCl_2$−$RECl_3$ was prepared through the following displacement reaction:

$$RE\ (s) + 3/2\ MgCl_2\ (l) = RECl_3\ (l) + 3/2\ Mg\ (l). \qquad (8)$$
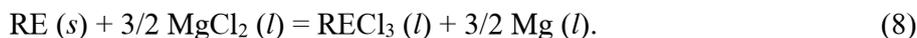
Approximately 50 g of silver shot (≥ 99.99 %, shot, Ijima Kingin Kogyo Co., Ltd.) was placed in the chamber to absorb the Mg generated during the displacement reaction and electrolysis. Approximately 20 g of Ti sponge (≥ 99 %, Toho Titanium Co., Ltd.) was placed to absorb the residual water and nitrogen contents in the flux. After the $MgCl_2$ was melted under an Ar atmosphere, the C rod anode (≥ 99.99 %, 6 mm in diameter, Nilaco Co., Ltd.) was inserted into the flux, and a pre-electrolysis was conducted. To carry out the pre-electrolysis, 2.2 V was applied for 43−86 ks between the Ti crucible and the C anode using a potentiogalvanostat (SI 1287, Solartron, Inc.) to discharge the residual O^{2-} in the flux.

After the pre-electrolysis, electrochemical deoxidation was carried out by applying a constant voltage between the Ti sample and C anode. The reaction time in a typical experiment is approximately 86 ks, as assessed based on the diffusion coefficient of O in β-Ti at high temperature [20]. In some of the experiments, MgO (≥ 98 %, powder, Wako Pure Chemical Industries, Ltd.) was added to the molten $MgCl_2$−$RECl_3$.

After the electrochemical deoxidation, the Ti cathodes were removed from the molten $MgCl_2$, cooled in a stream of Ar gas, and then removed from the reaction chamber. The flux attached to the surface of the Ti electrode was detached by leaching in an acetic acid solution. The Ti samples were cleaned using a (1 + 10) aqueous HCl solution followed by water, alcohol, and acetone, and then dried.

The concentration of oxygen in the Ti sample was measured using an inert gas-fusion technique (TC-600, LECO Co.). Prior to the analyses of the O concentration in the Ti samples, the Ti samples were chemically polished in a mixture of $HF:HNO_3:H_2O$ with a ratio of 1:4:10. To smoothly extract the oxygen, each 0.1 g of the Ti sample was melted using approximately 1 g of a high-purity nickel flux (Ni basket 502-344, LECO Co.) containing 4 ± 2 μg oxygen. Standard Ti samples containing 980 ± 40 mass ppm O (Ti pin 501-657, LECO Co.) were used for calibration during the oxygen analysis. The analysis errors of O and N concentrations in the Ti samples are due to the uncertainty of the calibration curve and the fluctuation of the measured total amount of oxygen in the Ni flux.

3. Results and Discussion

Figure 4 shows an E-pO^{2-} diagram, called a Littlewood diagram [17] for Mg-O-Cl and Y-O-Cl systems at 1,200 K superimposed over each other. This diagram is newly depicted at 1,200 K based on our previous study [3, 16]. Following the method proposed by Littlewood, the standard Gibbs energy of formation of oxide ion, $\Delta G^{\circ}_{f, O^{2-}}$, was calculated from the Gibbs energies of the formation of liquid $MgCl_2$ [4] and liquid MgO [18] ($\Delta G^{\circ}_{f,\ O^{2-}} = \Delta G^{\circ}_{f,\ MgCl_2(l)} - \Delta G^{\circ}_{f,\ MgO(l)}$). In this diagram, the equilibrium potential for the redox reaction between Cl_2 gas and Cl^- ion is set to zero. Because there are no reliable data for the activity coefficient of oxide ions in our system, to create the diagram, assuming that $a_{O^{2-}}$ obeys Raoult's law, the anion mole fraction of oxide ions, $x_{O^{2-}}$ ($x_{O^{2-}} = n_{O^{2-}} / (n_{O^{2-}} + n_{Cl^-})$, where n_i is mole of the constituent anion, i), is taken as the activity of oxide ions, $a_{O^{2-}}$. Furthermore, the activity of chloride ions is approximated as 1 because the main scope of this research is at a high pO^{2-} (i.e., low $a_{O^{2-}}$).

Mg metal forms at the cathode in $MgCl_2$−YCl_3 during electrochemical deoxidation. The Mg reduces the oxygen in Ti to O^{2-}. In this case, the concentration of oxide ions in the flux is decreased through the formation of YOCl and is maintained at a low level. Furthermore, the O^{2-} is removed from the system through the formation of carbon oxides at the anode when the applied voltage is higher than 1.6 V. A Cl_2 gas evolution also occurs at applied voltages of higher than 2.3 V. The dominant reaction is expected to be the evolution of Cl_2 at a low pO^{2-}.
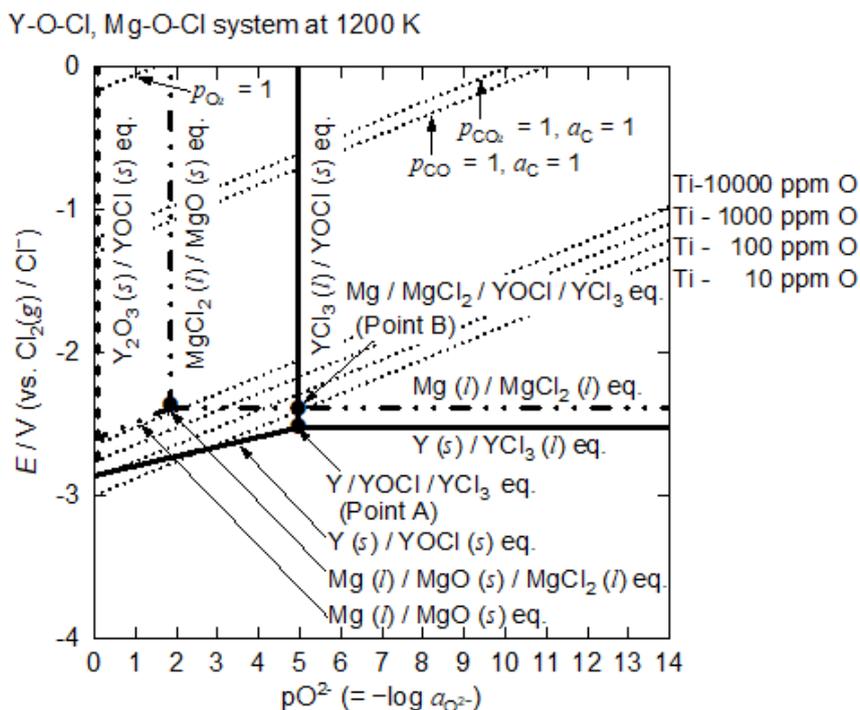
Fig. 4 E-pO^{2-} **diagram of M-O-Cl systems (M = Y, Mg) at 1,200 K ($\Delta G^{\circ}_{f,\,O^{2-}}$ = 33.1 kJ) [3, 4, 16, 17, 18].**

The oxygen and nitrogen contents in Ti samples that are electrochemically deoxidized in the $MgCl_2$−YCl_3 flux are summarized in Table 1 [16]. The oxygen content in the Ti decreased to approximately 100 mass ppm O. It is noteworthy that the oxygen content in β-Ti decreases to less than 500 mass ppm O even with the addition of MgO. When large amounts of Ti scrap are generated in the future, a deoxidation process in which large amounts of Ti scrap can be processed will be favorable. The proposed method, which decreases the O concentration in Ti to a level of less than 500 mass ppm O even when the molten salt is contaminated with O^{2-}, is attractive for practical application. Furthermore, the oxygen content in β-Ti also decreases to less than 1,000 mass ppm O in $MgCl_2$−$HoCl_3$ [12]. The values obtained using electrochemical deoxidation are much smaller than those obtained using thermochemical deoxidation in the flux under the same concentration [3, 11].

Table 1 Experimental conditions and deoxidation results of electrochemical deoxidation experiments [16].

Exp. no.	Composition of molten salt[a]	Experimental conditions[b]	Oxygen content, C_O (mass ppm O)		Nitrogen content, C_N (mass ppm N)		Maximum analysis error of oxygen content after exp. (%)	Maximum analysis error of nitrogen content after exp. (%)
			Initial[c]	After exp.[e]	Initial[c]	After exp.[e]		
180226-1	$MgCl_2$−YCl_3	1200 K / 86 ks 2.5 V / 0.3 A	1100	50, 110, 150	20	50, 50, 50	46	16
180417-5	$MgCl_2$−YCl_3−MgO[d]	1200 K / 84 ks 2.6 V / 2.4 A	1100	450, 360	20	70, 60	7	18

a: #180226 and #180417: $MgCl_2$-10 mol% YCl_3 (Total salt is about 550 g or 1100 g in a typical experiment.)
b: Average value of the applied current is noted.
c: Average value of analyzed initial oxygen content is noted.
d: 5.0 g MgO was added into molten salt.
e: Representative analytical conditions:
f: Standard sample: Ti pin ~0.1 g, 980 ± 40 mass ppm O, 130 ± 20 mass ppm N, part number: 501-657
   Ni flux: ~1.0 g, 4 ± 2 μg O, 0.0 ± 0.0 μg N, part number: 502-344.

In the past, the use of rare-earth metals for the recycling of Ti scrap was considered impractical. However, in recent years the situation has changed owing to the rapid growth and expected continuous growth in the production of rare-earth products such as a magnet for electric vehicles containing Nd and Dy [13, 15]. As the demand for Nd and Dy increases, the production of Y, La, and Ce are also increased as the by-products of Nd and Dy. However, the consumption of these rare-earth metals is expected to remain steady for a while [15], and thus the oversupply of some rare-earth metals is expected to occur [14].

Figure 5 shows the new process flow of recycling of titanium scrap proposed herein. With the development of the regeneration process of REOCl, this process achieves a zero emission of rare earth metals. By decreasing the production cost of Ti, Ti products will be commonly used in industry at a large-scale. If the demand for Ti rapidly increases, the amount of scrap generated will also grow accordingly. Thus, the development of recycling technologies for efficiently removing O from Ti scrap will become even more important.
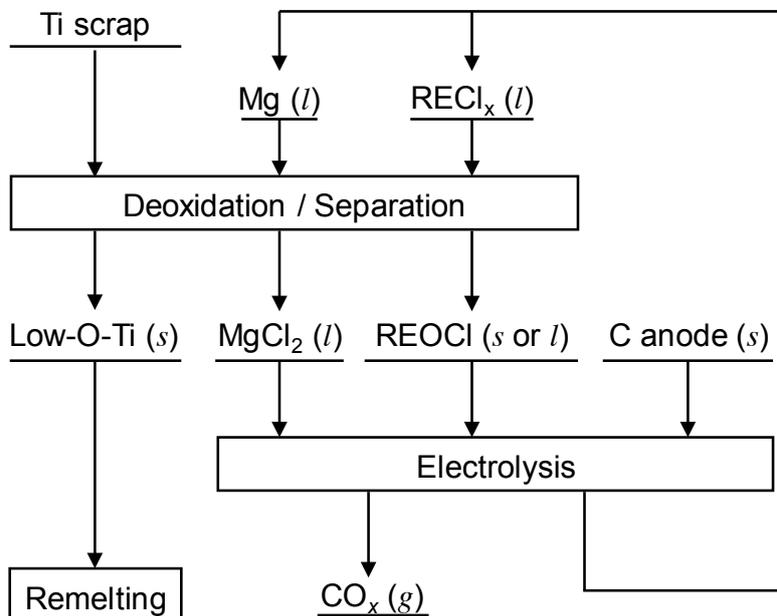

Fig. 5 New deoxidation process by utilizing Mg/MgCl₂/REOCl/RECl₃ equilibrium and the recovery process of deoxidation byproducts.

4. Conclusion

It has generally been considered impossible to deoxidize Ti at levels of 1,000 mass ppm O using Mg/MgO equilibrium owing to Mg's weak deoxidation capability. We developed a new deoxidation process that utilizes Mg as the deoxidizing agent in the mixture of a magnesium chloride and rare-earth chloride flux to decrease the deoxidation limit of Ti by decreasing a_{MgO} or the activity of oxide ion, $a_{\mathrm{O^{2-}}}$, in molten salt. To further decrease the oxygen content in the Ti, we developed a process for the electrochemical deoxidation of Ti in $\mathrm{MgCl_2-RECl_3}$, which decreases the oxygen content in Ti samples to approximately 100 mass ppm O, and to less than 500 mass ppm O with the addition of MgO. The results indicate that the new deoxidation process developed in this study can be applied to the recycling of large amounts of Ti scrap, which are expected to increase in the future.

5. Acknowledgement

6. References

[1]   T. Suzuki, Titanium Japan, 59 (2011) 203−209. (in Japanese).

[2]   O. Takeda and T. H. Okabe, JOM Journal of The Mineral, Metals & Materials Society (2018) doi.org/10.1007/s11837-018-3278-1.

[3]   C. Zheng, T. Ouchi, A. Iizuka, Y. Taninouchi, T. H. Okabe Metall. Mater. Trans. B. 50, (2019) 622−631.

[4]   I. Barin: Thermochemical Data of Pure Substance, 3rd Edition (Weinheim, Germany: Wiley-VCH, 1995).

[5]   Y. Taninouchi, Y. Hamanaka and T. H. Okabe Metall. Mater. Trans. B, 47 (2016) 3394−3404.

[6]   T. H. Okabe, Y. Hamanaka and Y. Taninouchi Faraday Discuss., 90 (2016) 109−126.

[7] M. Ito, K. Morita, The Solubility of MgO in Molten $MgCl_2$-$CaCl_2$ Salt, Mater. Trans., 45 (8) (2004) 2712–2718.

[8] T. H. Okabe, C. Zheng, Y. Taninouchi, Metall. Mater. Trans. B, 49 (2018) 1056–1066.

[9] T. H. Okabe, Y. Taninouchi, C. Zheng, Metall. Mater. Trans. B, 49 (2018) 3107–3017.

[10] T. H. Okabe, R. O. Suzuki, T. Oishi, and K. Ono, Mater. Trans. JIM, 32 (1991) 485–488.

[11] L. Kong, T. Ouchi, T. H. Okabe, Mater. Trans., 60, (9) (2019) 2059–2068.

[12] L. Kong, T. Ouchi, T. H. Okabe, J. Electrochem. Soc., accepted in press.

[13] H. Tamamura, J. Surf. Finish. Soc. Jpn, 60 (2009) 474–479 (in Japanese).

[14] E. Nakamura, Molten Salts, 58 (2015) 119–126 (in Japanese).

[15] Rare Earths: Global Industry, Markets and Outlook to 2026, 16th Edition, 2016, Roskill Information Services, London, UK, 2016.

[16] C. Zheng, T. Ouchi, L. Kong, Y. Taninouchi, T. H. Okabe, Metall. Mater. Trans. B, 50 (2019) 1652–1661.

[17] R. Littlewood, J. Electrochem. Soc., 109 (1962) 525–534.

[18] M. W. Chase, NIST-JANAF Thermochemical Tables, 4th Edition (American Institute of Physics, 1998).

[19] Y. B. Patrikeev, G. I. Novikov and V. V. Badovskii, Russ. J. Phys. Chem., 47 (1973) 284.

[20] C. J. Rosa, Metall. Trans., 1 (1970) 2517–2522.