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Direct oxygen removal technique for recycling titanium using molten MgCl₂ salt

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Deoxidation of Ti, or direct removal of O dissolved in metallic Ti, is known to be extremely difficult when Mg is used as the deoxidizing agent. This difficulty arises because the chemical potential of O_2, p_{O_2}, under Mg/MgO equilibrium is high (approximately 10^{-41} atm at 1200 K) and is equivalent to that of Ti containing ~2 mass% O at 1200 K. Therefore, when deoxidizing Ti to the commercial level of high-grade pure Ti (below 0.05 mass% O) using an Mg reductant at 1200 K, the activity of the reaction product MgO (a_{MgO}) must be decreased to below ~0.025, which is difficult in practice. In this study, the removal of O in Ti in molten MgCl₂ salt using an electrochemical technique was examined at ~1173 K with the objective of obtaining Ti containing less than 0.05 mass% O. Ti samples and graphite electrodes immersed in molten MgCl₂ served as the cathode and anode, respectively. A constant voltage was applied between the electrodes using an external DC source. Molten MgCl₂ was employed to produce the deoxidizing agent Mg and to facilitate deoxidation of Ti by decreasing the activity of the reaction product MgO. By applying a voltage of approximately 3.1 V between the electrodes, the chemical potential of Mg in the molten MgCl₂ was increased at the surface of the Ti cathode, and the Ti samples were deoxidized. The resulting O species, mainly formed O^{2-} dissolved in the molten MgCl₂, was removed from the molten salt by reacting with the C anode to form CO (or CO₂) gas. Ti wires containing 0.12 mass% O were deoxidized to less than 0.02 mass% O. In some cases, the O concentration in the Ti samples was reduced to the level of 0.01 mass%, which cannot be accomplished using the conventional Kroll process. The possible application of this deoxidation technique to practical industrial recycling processes is discussed.

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Introduction

In recent years, the recycling of Ti and Ti alloys has become an important issue.[1,2] The demand for Ti and Ti alloys in the aerospace industry is increasing, and large amounts of Ti scraps are generated from the fabrication of Ti and Ti alloy products. Fig. 1 shows the material flow of Ti in the US.[1] The volume of scrap generated is greater than the volume of fabricated Ti products.

Commercial Ti and its alloys contain oxygen at approximately 0.1 mass% (1000 mass ppm) as a major impurity. Oxygen contamination of the product must be avoided, because the presence of O deteriorates the mechanical properties of the metals. Table 1 shows the ASTM grades and acceptable impurity concentrations of Ti and its alloys.[3] In producing commercially pure Ti of ASTM Gr. 1, low-O-containing Ti feed such as high-purity Ti sponge (0.03–0.1 mass% O) produced by the Kroll process[4] is used. Using large amounts of scrap metal to produce low-O Ti is hindered by the high O level in Ti scrap, which typically exceeds 0.1 mass%. Titanium and its alloys containing more than 0.4 mass% O cannot be recycled into titanium alloys, and these metals are mainly used in cascade recycling as additive elements for steel, aluminum, *etc.*

O removal directly from Ti and its alloys to levels below 0.1 mass% (1000 mass ppm) is very difficult because O dissolves in Ti to form an interstitial solid solution, and because Ti has a strong affinity with O.[5,6] Table 2 lists some effective methods for direct removal of O from Ti and from TiAl.[2,6–48] For example, the deoxidation of solid Ti by reaction with chemically active Ca dissolved in $CaCl_2$ in the temperature range of 1273 to 1473 K has been examined. Okabe *et al.* successfully produced Ti containing less than 50 ppm by mass of O with a high residual resistivity ratio (RRR > 120).[18,19] Ca metal is one of the most effective deoxidation agents because it has an extremely strong affinity for O and because it
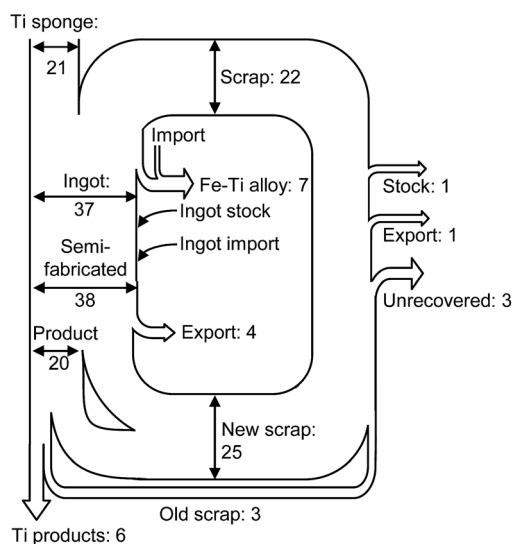

Fig. 1 Estimated material flow of titanium scrap in the U.S. in 2004.[1] Units in the figure are 10^3 ton. Values are rounded to the nearest thousand metric tons of contained titanium.
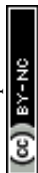
Table 1 Grades and impurity concentrations of pure titanium and titanium alloys[3]

		Concentration of element i, C_i (mass%)						
	Specification	C	H	O	N	Fe	Al	V
Pure Ti	ASTM Gr. 1	≤0.08	≤0.015	≤0.18	≤0.03	≤0.2	—	—
	ASTM Gr. 2	≤0.08	≤0.015	≤0.25	≤0.03	≤0.3	—	—
	ASTM Gr. 3	≤0.08	≤0.015	≤0.35	≤0.05	≤0.3	—	—
	ASTM Gr. 4	≤0.08	≤0.015	≤0.40	≤0.05	≤0.5	—	—
Ti–Al–V alloy	ASTM Gr. 5	≤0.08	≤0.015	≤0.20	≤0.05	≤0.40	5.5–6.75	3.5–4.5
	ASTM Gr. 23	≤0.08	≤0.0125	≤0.13	≤0.03	≤0.25	5.5–6.5	3.5–4.5

has very low solubility in solid Ti. In the Ca-halide flux deoxidation process shown in Table 2, the $CaCl_2$ flux contains the deoxidation agent Ca and facilitates the reaction by diluting the reaction product CaO, thus decreasing the activity of the by-product. However, the purity of flux and the initial O content of the Ti are subject to limits, since the ultimate limit of deoxidation depends on the amounts of both O present as an impurity in the $CaCl_2$ flux and CaO produced during deoxidation.

An effective technique for the preparation of O-free Ti by electrochemical deoxidation using $CaCl_2$ molten salt has been developed.[21] Removal of O^{2-} (present as CaO in the flux) and production of Ca deoxidant using electrochemical techniques improved the deoxidation limit of the Ca-halide flux deoxidation process. Under certain conditions, Ti with 0.001 mass% (10 mass ppm) O has been successfully produced by the electrochemical deoxidation technique.

Hashimoto *et al.* proposed a method for the deoxidation of Ti during electrowinning using molten fluoride salt baths,[45–47] but contamination of Ti by O or C is unavoidable using this method. In 2001, Chen *et al.* developed a novel process, called the FFC process, for producing Ti directly from TiO_2 immersed in $CaCl_2$ molten salt using electrochemical methods, and they succeeded in obtaining low-O Ti using this process.[26–28] Ono and Suzuki developed a new Ti reduction process that utilizes electrochemically produced Ca reductant in molten $CaCl_2$ salt.[32] To obtain low-O Ti, a highly reducing atmosphere is required. For this reason, molten $CaCl_2$ with high metallic Ca activity is employed as the reaction medium. Other recent developments in deoxidation techniques for Ti and its alloys are also listed in Table 2.

Deoxidation of Ti using Mg as the deoxidizing agent is believed to be almost impossible. This is because the deoxidation limit of a Ti–O solid solution by Mg under MgO saturation is about 2 mass% (20 000 mass ppm) at 1200 K; reducing the deoxidation limit to the level of 100 mass ppm is difficult from a practical perspective. However, if deoxidation of Ti using a $MgCl_2$ medium becomes feasible, the reduction and electrolysis facilities of the conventional Kroll process[4] could be utilized. Therefore, developing an effective deoxidation process for Ti and its alloys using molten $MgCl_2$ is expected to significantly enhance the recovery rate for Ti scraps and the production of low-O-containing Ti.

Table 2 Some examples of the upgrading process for titanium metal investigated in previous studies[2,6–48]

Method	Reference	Advantages (deox. limit)	Disadvantages
Deoxidation (Deox.)			
Deox. by M/MOx eq. (DOSS process)	Ono and Miyazaki,[6] Fisher,[7–10] Okabe et al.,[11–14] Oh et al.,[15,16] Roh et al.[17]	Ti powder can be deoxidized. ($\sim$500 ppm O)	Low capability of deox.
Calcium halide flux deox.	Okabe et al.[18–20]	High capability of deox. ($\sim$50 ppm O)	Not suitable for removing large amounts of O. Leaching of molten salt bath is needed
Electrochemical deox.	Okabe et al.,[21,22] Nakamura et al.,[23] Hirota et al.,[24] Taninouchi et al.[25]	Ultra-high capability of deox. $CaCl_2$ bath (<10 ppm O), $MgCl_2$ bath (<100 ppm O)	Long processing time
FFC process	Chen et al.,[26–28] Fray,[29] Mohandas and Fray,[30] Tripathy et al.[31]	Production of low-oxygen titanium directly from oxides	Long processing time
OS process	Ono and Suzuki,[32] Suzuki et al.[33–37]	Production of low-oxygen titanium directly from oxides	Long processing time
Deox. during EB remelting with Al	Yahata et al.[38]	Short processing time ($\sim$100 ppm O)	Excess Al is contained in Ti
VIM with $CaAl_2$	Rotmann et al.[2]	Short processing time ($\sim$1500 ppm O)	Capability of deox. is insufficient
PESR with Ca and CaF_2 flux	Reitz et al.[39]	Short processing time ($\sim$250 ppm O)	Subsequent VAR is required to remove residual Ca. Applicability to deoxidation of pure Ti is uncertain
Electric arc remelting under H_2–Ar atmosphere	Su et al.[40]	Short processing time ($\sim$300 ppm O)	Capability of deox. is insufficient. Applicability to deoxidation of pure Ti is uncertain
Deox. of Ti alloy by HDH	Oh et al.,[16] Roh et al.[17]	Simple process	Capability of deox. is insufficient
Others			
Electrorefining in molten salt	Nettle et al.,[41] Suchkov et al.,[42] Takeuchi et al.,[43,44] Hashimoto et al.,[45–47] Miyazaki et al.[48]	Almost all impurities can be removed	Contamination from molten salt. Difficulty of morphology control of Ti deposition

Table 3 Some representative results for titanium deoxidation using various solid state deoxidation techniques

| Method[a] | Oxygen (mass ppm) | | Nitrogen[c] (mass ppm) | | Note and references |
	Init.	After deox.	Init.	After deox.	(Exp. no.)
Ca-CaO	430 →	460	20 →	340	1273 K, 86 ks, ref. 11
	1430 →	470	100 →	470	Eqn (3)
Y-Y$_2$O$_3$	200 →	120	N.A.[f]		1231 K, 260 ks, ref. 12
	1100 →	150, 170	N.A.[f]		(#2U)
Y-Y$_2$O$_3$	210 →	90	10 →	(30)	1213 K, 551 ks, ref. 14
	950 →	100, 220	20 →	(50)	(#U)
	670 →	80, 100	30 →	(60)	
Y-Y$_2$O$_3$	210 →	40, 80	10 →	(50)	1173 K, 518 ks, ref. 14
	950 →	160, 160	20 →	(120)	(#T)
	670 →	30, 240	30 →	(80)	
Ca-Y-Y$_2$O$_3$	210 →	130	10 →	(40)	1173 K, 604 ks, ref. 14
	950 →	60, 90	20 →	(50)	(#W)
	670 →	60, 90	30 →	(120)	
Ca-CaCl$_2$	130 →	16	10 →	41	1273 K, 90 ks, ref. 19
	130 →	17	10 →	34	(#17B1)
					RRR$_{4.2}$[d] = 98, Hv[e] = 85
Ca-CaCl$_2$	130 →	35	10 →	49	1373 K, 40 ks, ref. 19
	130 →	22	10 →	45	(#19B1)
					RRR$_{4.2}$[d] = 95, Hv[e] = 92
Ca-CaCl$_2$	150 →	62	10 →	86	1273 K, 86 ks, ref. 19
					(#3C)
					RRR$_{4.2}$[d] = 122, Hv[e] = 82
Electrochem. (CaCl$_2$)[b]	900 →	<10	40 →	20	1223 K, 22 ks, ref. 21
	1400 →	<10	20 →	20	(#49, contaminated by carbon)
Electrochem. (CaCl$_2$)[b]	110 →	10	<10 →	<10	1223 K, 27 ks, ref. 23
	900 →	20	30 →	50	(#69, carbon: 20 → 30, 50 → 80 ppm)
					RRR$_{4.2}$[d] = 155, Hv[e] = 64
Electrochem. (CaCl$_2$)[b]	210 →	40, 50	10 →	10	1189 K, 36 ks, ref. 24 (#12)
	(O in Gd: 2100 → 10, 50 ppm, O in Tb: 2600 → 20, 20 ppm, O in Dy: 2300 → 20, 30 ppm O in Er: 2800 → 40, 40 ppm, O in Y: 11200 → 340, 380 ppm)				
Electrochem. (MgCl$_2$)[b]	110 →	100	<10 →	40	1173 K, 86 ks, ref. 23
	900 →	60	30 →	70	(#75, carbon: 20 → 50, 50 → 120 ppm)
	840 →	90	20 →	440	1173 K, 86 ks, ref. 25 (D13_150121[g])
	1200 →	270	40 →	260	1173 K, 86 ks, ref. 25 (D15_150123[h])

[a] "M-MOx": deoxidation by metal/metal oxide, "Ca-CaCl$_2$": calcium-halide flux deoxidation, "Electrochem.": electrochemical deoxidation. [b] Salt in parentheses shows molten salt used for electrochemical deoxidation. [c] Values in parenthesis include uncertainties. [d] Residual resistivity ratio, $\rho_{298}/\rho_{4.2}$, determined by measurement at 298 and 4.2 K. [e] Vickers micro hardness (kg f mm^{-2}), measured using 500 g load at room temperature. [f] "N.A.": not analyzed or not reported. [g] Ti wire (ϕ1.0 mm) was used as sample. Oxygen and nitrogen contents were analyzed by KOBELCO Research Institute, Inc. [h] Ti rod (ϕ3.0 mm) was used as sample. Oxygen and nitrogen contents were analyzed by KOBELCO Research Institute, Inc.
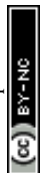
Principle

Because the principle of electrochemical deoxidation of Ti has been reported in detail previously,[5,21] the deoxidation process is only briefly outlined here. A solid Ti–O solution is deoxidized by Mg in the following reaction:

$$O \text{ (in Ti)} + Mg \text{ (in flux)} = MgO \text{ (in flux)} \tag{1}$$

The equilibrium O concentration in Ti depends thermodynamically on the temperature T according to the following equation,

$$[\text{mass\% O}] = (a_{MgO}/a_{Mg})(1/f_O)\exp(\Delta G^\circ/RT) \tag{2}$$

where ΔG° is the standard Gibbs free energy change associated with the reaction described by eqn (1), a_{MgO} and a_{Mg} are the activities of MgO and Mg, respectively, and f_O is the activity coefficient of O in solid Ti.

Fig. 2 shows the binary phase diagram for the Ti–O system.[49] The equilibrium O concentration of Ti under Mg/MgO equilibrium at 1273 K is plotted as an open circle. For reference, the equilibrium O concentration of Ti under Ca/CaO equilibrium at 1273 K is plotted as a filled circle (about 0.05 mass% O). The equilibrium O concentration under Mg/MgO equilibrium is approximately 2.6 mass% (7.4 mol%) at 1273 K. This shows that it is thermodynamically difficult to remove O directly from Ti to levels below 1 mass% by Mg deoxidant when the activity of MgO (a_{MgO}) is high.

The O potentials of β-Ti–O solid solution at temperatures between 1173 and 1473 K have been determined,[11] and the feasibility of preparing low-O Ti by decreasing the activity of the by-product CaO (a_{CaO}) has been examined using various Ca-halide fluxes in the presence of Ca metal (Ca-halide flux deox. shown in
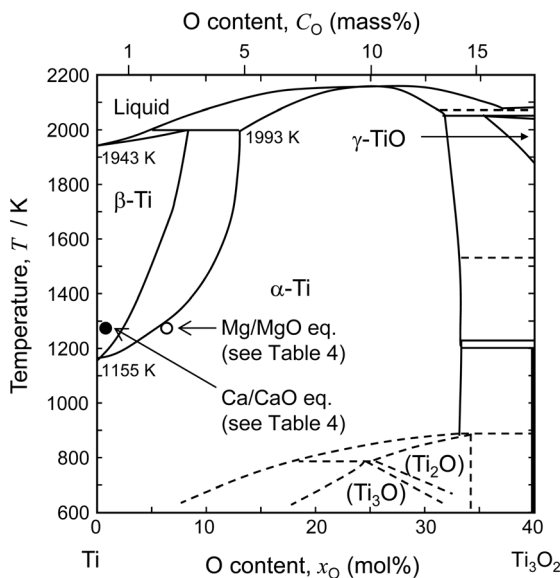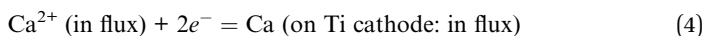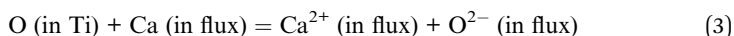

Fig. 2   Phase diagram of the Ti–O binary system.[49] Compositions of Ti–O solution under Ca/CaO and Mg/MgO equilibrium at 1273 K are plotted in the figure.

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Table 2).[18,19] Several factors have been considered in selecting a flux for deoxidation. $CaCl_2$ has been found to be the most desirable flux at temperatures of ~1300 K because the deoxidation product CaO dissolves easily in $CaCl_2$ flux, which decreases its activity and thus lowers the limit of deoxidation. By submerging Ti wires and small pieces in Ca-saturated $CaCl_2$, Ti samples has been deoxidized to a level of 50 mass ppm (see also Table 3).[5,19]

In the Ca-halide flux deoxidation method, the ultimate limit of deoxidation depends on the final O concentration in the flux, which means that the purity of the flux and the initial O content of the Ti will rule the deoxidation limit. To decrease the deoxidation limit set by a_{CaO}, an electrochemical method was developed (electrochemical deox. shown in Table 2).[21,22] The modified Ca-halide flux deoxidation method is characterized by both the production of Ca from the $CaCl_2$ flux and the effective removal of O^{2-} (present as CaO) dissolved in the flux by electrochemical means. In this method, as expressed in eqn (3), a Ti cathode is deoxidized by Ca, which forms electrochemically on the surface of the cathode according to eqn (4). O^{2-} species in the flux are carried continuously to the C anode, and O in the flux is removed from the system as CO (or CO_2) gas by the anodic reaction expressed in eqn (5).

$$O \text{ (in Ti)} + Ca \text{ (in flux)} = Ca^{2+} \text{ (in flux)} + O^{2-} \text{ (in flux)} \tag{3}$$

$$Ca^{2+} \text{ (in flux)} + 2e^- = Ca \text{ (on Ti cathode: in flux)} \tag{4}$$

$$O^{2-} \text{ (in flux)} + C \text{ (C anode)} = CO \text{ (gas)} + 2e^- \tag{5}$$

Unlike the Ca-halide flux deoxidation, the electrochemical method does not require the addition of metallic Ca as a deoxidant, because the activity of Ca near the cathode can be increased by controlling the applied voltage between the Ti cathode and the C anode. In some cases, Ca is precipitated on the cathode using an applied voltage exceeding the theoretical decomposition voltage of $CaCl_2$ (3.25 V at 1223 K). Furthermore, $CaCl_2$ flux can be purified through pre-electrolysis. This electrochemical method therefore has the advantage that contamination-free Ca deoxidant and $CaCl_2$ flux can be used in the deoxidation process. By applying the electrochemical technique to molten $CaCl_2$, Ti containing O below 10 mass ppm has been successfully produced under certain conditions.[5,21]

In this study, the feasibility of the electrochemical deoxidation technique using $MgCl_2$ as flux was examined. A schematic of the electrochemical deoxidation of Ti in molten $MgCl_2$ is shown in Fig. 3.

$$O \text{ (in Ti)} + Mg \text{ (in flux)} = Mg^{2+} \text{ (in flux)} + O^{2-} \text{ (in flux)} \tag{6}$$
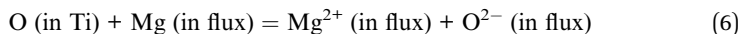
Based on the thermodynamic calculation shown in Fig. 4,[5,11,50] when a_{MgO} is decreased to the level of 10^{-2} in the presence of metallic Mg at 1200 K, the chemical potential of O_2 (p_{O_2}) in the system is decreased to ~10^{-45} atm, and Ti containing 0.018 mass% (180 mass ppm) O can be obtained. In other words, when Ti is deoxidized down to commercial O levels for high-grade Ti (0.05 mass% O, or 500 mass ppm) using Mg as reductant, a_{MgO} at 1200 K must be decreased to the level of 0.025.
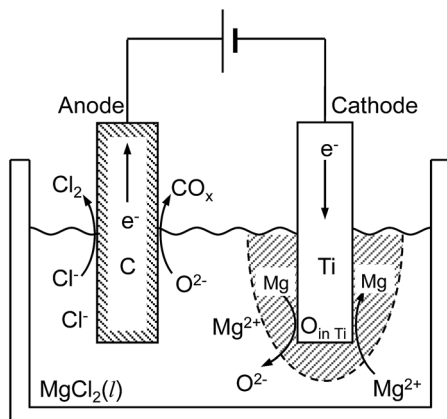
Fig. 3 Schematic illustration of electrochemical deoxidation in MgCl$_2$ molten salt. Electrolysis is achieved using titanium as the cathode and carbon as the anode. At the cathode, a deoxidant of magnesium is produced by electrolysis, and the deoxidation product of magnesium oxide is dissolved in molten salt. At the anode, an oxide anion generated by the cathode is removed as carbon monoxide or dioxide gas. The anode reaction occurs in parallel with chlorine evolution. During this process, the activity of MgO can be kept at a low level on the cathode surface.
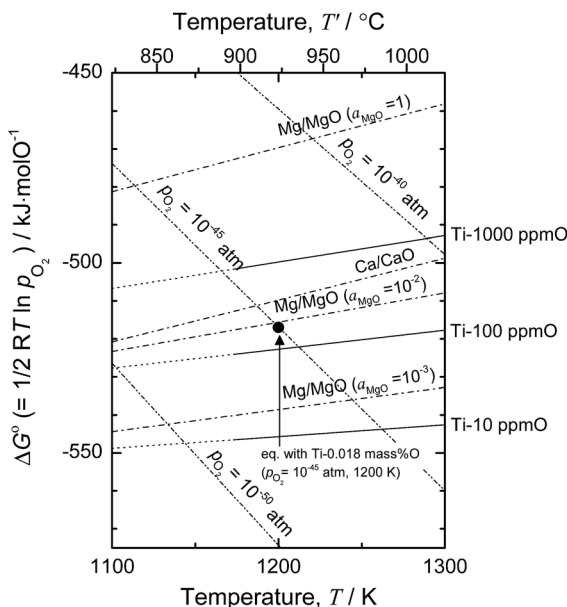
Fig. 4 Ellingham diagram of selected oxides[50] and solid solutions of Ti–O.[5,11] Oxygen chemical potential for Ti-0.018 mass% O ($p_{O_2} = 10^{-45}$ atm) at 1200 K is plotted for reference.

Experimental procedure

Fig. 5 shows a flowchart of the experimental procedure for the electrochemical deoxidation of Ti in MgCl$_2$. A schematic of the experimental apparatus used for
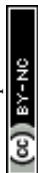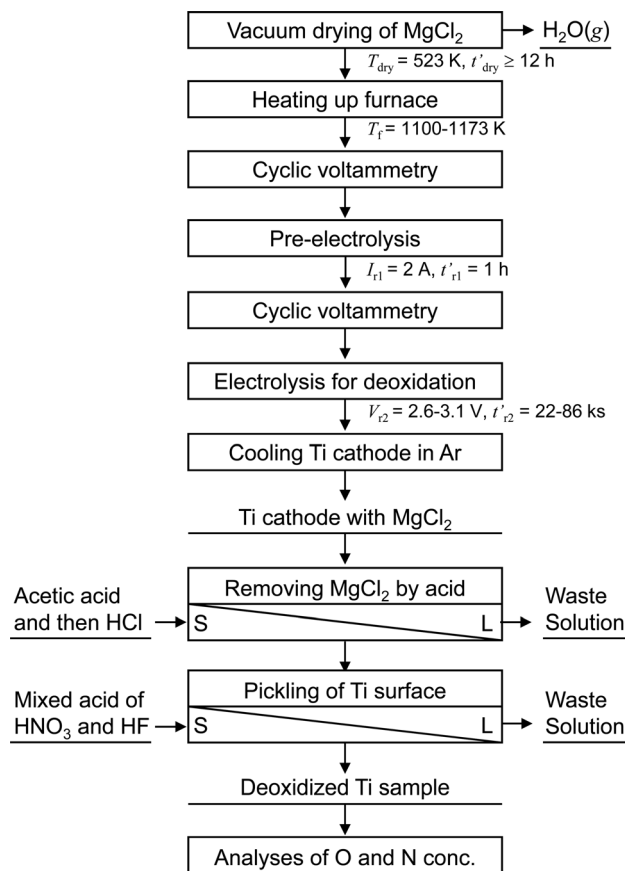
Fig. 5 Flowchart of experimental procedure for electrochemical deoxidation of titanium in molten MgCl₂.

the electrochemical deoxidation of Ti in $MgCl_2$ is shown in Fig. 6. Ti in the form of small pieces and wires with different O concentrations and configurations was used as the starting material. The flux was reagent-grade anhydrous $MgCl_2$ (>97.0%) in flake form, dried at 523 K for more than 43 ks (12 h).

The dehydrated $MgCl_2$ flux was contained in a Ti or mild steel crucible (89 mm in diameter, 200 mm in height) and set in a gas-tight stainless steel chamber, as shown in Fig. 6. The Ti cathode consisted of several strands of Ti wire ~50 mm in length and 1 mm in diameter. The total electrode surface area was approximately 1000 mm². In the same experiment, a Ti rod (approximately 30 mm in length, 3 mm in diameter) was used as the cathode. High-purity (99.9%) graphite was used as the C anode (approximately 35 mm in length, 3 or 6 mm in diameter). These electrodes, as well as thermocouple tubing, were inserted into the reaction tube through a gas-tight water-cooled stainless steel head.

After the assembled cell was evacuated at ~673 K to ensure a completely gas-tight and moisture-free system, Ar was introduced to the reaction tube. The furnace was then heated to a constant temperature between 1100 and 1173 K. After the $MgCl_2$ was melted, the graphite anode was inserted into the molten salt,
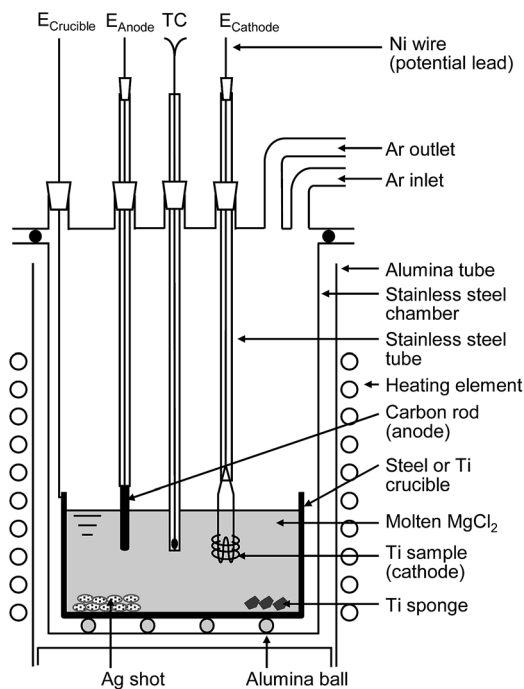
Fig. 6 Schematic illustration of experimental apparatus for electrochemical deoxidation of titanium in $MgCl_2$.

and pre-electrolysis was conducted. In the pre-electrolysis, a 2 A current was passed for ~3.6 ks (1 h) between the Ti crucible (or Ni electrode immersed in molten salt) and the C anode to eliminate residual metal and gaseous impurities in the molten salt. Approximately 50 g of silver was placed at the bottom of the crucible to absorb the magnesium metal deposited during electrolysis. The temperature of the molten salt was measured directly using a chromel–alumel thermocouple protected by a stainless steel sheath. After pre-electrolysis, the Ti cathode containing the Ti samples was inserted into the molten $MgCl_2$, and deoxidation experiments were performed by applying voltages between 0 and 3.1 V between the electrodes, which were separated by a distance of ~30 mm. In most cases, the deoxidation of the Ti cathode occurred with the application of voltages exceeding 2.6 V at 1100–1173 K for longer than 22 ks (6 h).

Before and after the pre-electrolysis of $MgCl_2$ and the deoxidation experiments, the electrochemical properties of the flux were measured by cyclic voltammetry (CV). An electrochemical interface (Solartron SI1287) was used for the CV measurements.

After the deoxidation experiment, the electrodes were removed from the molten $MgCl_2$, and the cell was cooled in a stream of Ar gas. In some cases, only the Ti cathode was replaced after cooling for the next experimental run. The fused salt that adhered to the surface of the Ti electrode was removed by leaching with (1 + 1) acetic acid, after which the Ti samples of the electrode were carefully

cleaned in (1 + 10) aqueous HCl solution, followed by water, alcohol, and acetone, and then dried.

The Ti samples obtained were subjected to O and N analyses using LECO analyzers. Prior to the analyses, the samples were surface-etched with a 1 : 4 : 10 mixture of HF–HNO$_3$–H$_2$O. To increase the accuracy of the O and N analyses, 1.1 g of nickel capsule containing 8.8 ± 1.4 µg O and 0.2 ± 0.2 µg N was used as an extraction bath for each 0.05–0.1 g Ti sample. The instrument for the O analysis was calibrated using Ti standard samples containing 470 ± 30 and 980 ± 40 mass ppm O.

Results and discussion

Fig. 7(a) shows the CV of the MgCl$_2$ salt at 1173 K using a Ni quasi-reference before pre-electrolysis. The deposition of Mg occurs at approximately −0.7 V with respect to the Ni quasi-reference, and gas evolution occurs at approximately +1.6 V. The
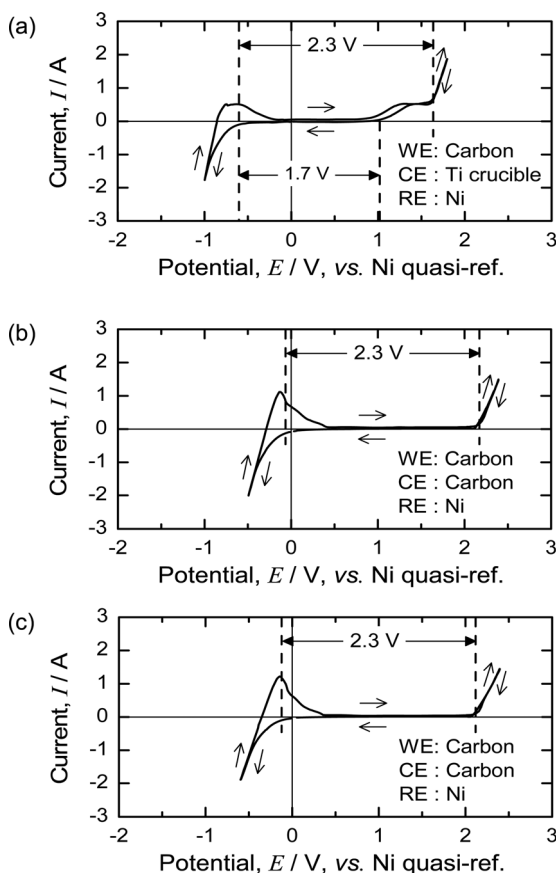

Fig. 7 Cyclic voltammograms in MgCl$_2$ molten salt at 1173 K. Surface area of electrode: 2 cm^2 (C rod, Ni rod). Surface area of electrode: 260 cm^2 (Ti crucible). Scan rate: 100 mV s^{-1}. (a) Before pre-electrolysis. (b) After pre-electrolysis. (c) After electrolysis for Ti deoxidation.

oxidation wave between 1 and 1.6 V probably results from oxygen impurities in the molten salt, and the gas evolution peak at $\sim$1.6 V corresponds to the evolution of Cl_2 gas.

During pre-electrolysis using a Ni electrode as a cathode, Mg metal was electrochemically deposited on the Ni electrode. After pre-electrolysis, the Mg deposition and gas evolution peaks shifted to 0 and 2.3 V, respectively. Fig. 7(b) and (c) show the CV of the molten $MgCl_2$ before and after the deoxidation experiments. As the theoretical decomposition voltage of $MgCl_2$ at 1173 K is 2.3 V,[50] the reference electrode worked correctly, and the Ni quasi-reference electrode became a reference for Mg/Mg^{2+} after pre-electrolysis.

The results shown in Fig. 7 indicate that the electrochemical properties of $MgCl_2$ are unchanged before and after the deoxidation experiments. After pre-electrolysis, only the Mg deposition wave and Cl_2 evolution are observed, and therefore, the reaction system in the molten salt can be regarded as contamination-free $MgCl_2$.

By applying a voltage of $\sim$3.1 V between the electrodes, the chemical potential of metallic Mg (a_{Mg}) in $MgCl_2$ was increased on the surface of the Ti cathode to a value approaching 1, and the Ti samples were deoxidized by the electrochemically produced Mg. The resulting O species, present mainly as O^{2-} dissolved in the molten $MgCl_2$, reacted at the C anode to form CO (or CO_2) gas, which was removed from the molten salt system. For example, after electrochemical deoxidation at 1173 K for 86 ks, Ti wires 1.0 mm in diameter and containing 0.084 mass % (840 mass ppm) O were deoxidized to 0.009 mass% (90 mass ppm) (Exp. no. D13_150121 shown in Table 3).[25] When a Ti rod of 3.0 mm diameter containing 0.12 mass% (1200 mass ppm) O was deoxidized at 1173 K for 86 ks, Ti with 0.027 mass% (270 mass ppm) O was obtained (Exp. no. D15_150123 shown in Table 3).[25] The N concentration in the sample was increased from $\sim$10–40 to 40–440 mass ppm after deoxidation.

In Table 3, some representative analytical results for the O and N levels in Ti before and after deoxidation are listed, as well as results from previous studies.[11,12,14,19,21,23–25] The analytical values below 0.01 mass% (100 mass ppm) listed in the table include some uncertainty because gas analysis of Ti samples below 0.01 mass% (100 mass ppm) is difficult. However, notably, Ti with an oxygen level of about 0.01 mass% (100 mass ppm) was obtained by using Mg as the deoxidant when using the electrochemical technique.

Table 4 summarizes the deoxidation limits for the Mg/MgO, Ca/CaO, and Y/Y_2O_3 systems. The activity of the metal oxides for obtaining Ti with 100 mass ppm O when using the respective metal deoxidants was calculated using the available thermodynamic data[11,50] and are listed in the table. In this study, Ti wires containing 0.12 mass% (1200 mass ppm) O were deoxidized to less than 0.02 mass% (200 mass ppm) O. In some cases, the O concentration in the Ti samples was reduced to below 0.01 mass% (100 mass ppm) O, which cannot be accomplished using the current Kroll process. These experimental results show that the activity of MgO, a_{MgO}, was decreased to below 0.01.

When electrolysis in $CaCl_2$ is utilized to remove O directly from Ti, the deoxidation limit can be easily decreased to below 0.01 mass% (100 mass ppm). However, after deoxidation, $CaCl_2$ flux attached on the surface of Ti products must be removed by dissolving in aqueous solution, which causes O pickup. It is
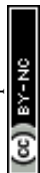
Table 4 Equilibrium oxygen concentrations calculated under M/MOx equilibrium at 1273 K using available thermodynamic data.[11,50] Calculated activities of metal oxides (a_{MO_x}) used to obtain low-oxygen-containing titanium (100 and 1000 mass ppm O) are also shown for reference

System	Equilibrium O conc. in Ti at 1273 K, $C_{O,eq}$ (mass ppm)	Required a_{MO_x} to obtain Ti with 1000 ppm O at 1273 K, a_{MO_x}	Required a_{MO_x} to obtain Ti with 100 ppm O at 1273 K, a_{MO_x}
Mg/MgO	26 000	0.039	0.0039
Ca/CaO	500	2.0	0.20
Y/YO$_{1.5}$	180	13	0.41

impractical to remove CaCl$_2$ by evaporation, because the vapor pressure of CaCl$_2$ is low even at elevated temperatures. Fig. 8 shows the temperature dependence of the vapor pressures of CaCl$_2$ and MgCl$_2$.[50] The vapor pressure of MgCl$_2$ is two or three orders of magnitude higher than that of CaCl$_2$. The high vapor pressure of MgCl$_2$ might enhance operational challenges during electrolysis.[51] However, MgCl$_2$ can be removed directly from titanium products by vacuum treatment; a technique for MgCl$_2$ removal *via* vacuum distillation is already established in the Kroll process. This MgCl$_2$ removal technique can easily be applied to the deoxidation process investigated in this study.

Fig. 9 shows the new recycling process for Ti scrap using electrochemical deoxidation in molten MgCl$_2$ followed by the removal of MgCl$_2$ by vacuum distillation. The reduction chamber used in the conventional Kroll process can be utilized in the electrochemical deoxidation process, as schematically shown in
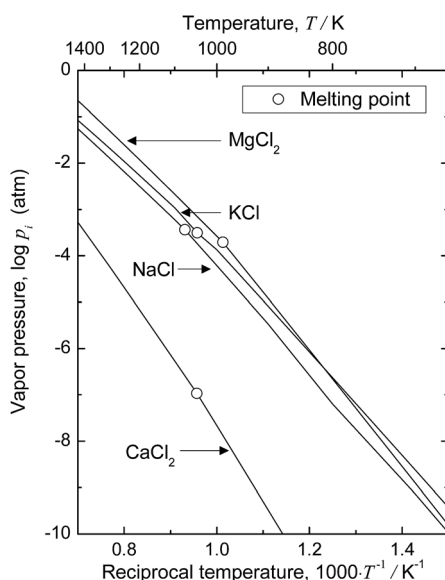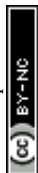

Fig. 8 Vapor pressures of metal chlorides as functions of reciprocal temperature.[50]
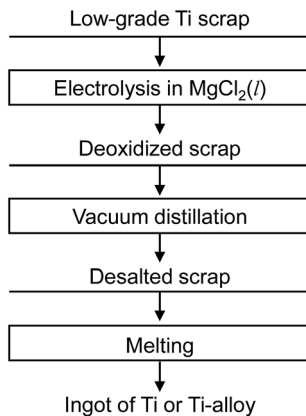
Fig. 9 Recycling process proposed in this study. Oxygen dissolved in Ti scrap is directly removed by molten salt electrolysis in $MgCl_2$.

Fig. 10. As Ti production is increased, scrap treatment becomes increasingly important. In the future, the direct O removal technique proposed in this study may be applied to recycling Ti scrap.
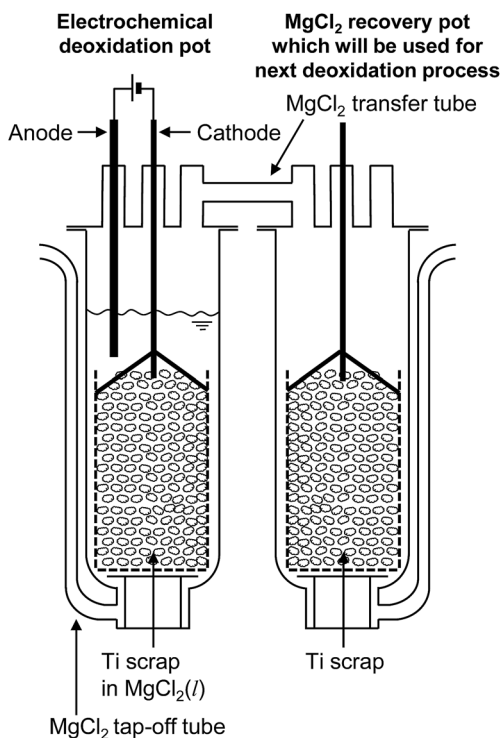

Fig. 10 Industrial application of the recycling process based on electrolysis in $MgCl_2$. Process is feasible in existing Ti smelters based on the Kroll process.

Conclusions

The removal of O from Ti using an electrochemical technique in molten $MgCl_2$ was examined at temperatures of ~1173 K. The activity of Mg was increased near the Ti cathode surface and the activity of MgO was decreased by applying voltages between the Ti cathode and C anode immersed in molten $MgCl_2$. These activity changes facilitated the deoxidation of a Ti cathode consisting of the Ti samples. A Ti sample containing approximately 1000 mass ppm O were deoxidized to less than 200 mass ppm by applying 3.1 V between the Ti and C electrodes for 86 ks. In some cases, the O concentration in Ti was decreased to below 100 mass ppm, which cannot be accomplished using the conventional Kroll process. The application of this deoxidation technique to industrial recycling processes may become practical in the future.

Acknowledgements

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