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Development of deoxidation process for off-grade titanium sponge using magnesium metal with wire mesh strainer type of crucible

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In this study, the deoxidation process for off-grade titanium (Ti) sponge using magnesium (Mg) metal with a wire mesh strainer type of crucible was developed. Ti hydride (TiH_2) feedstock, which was prepared by hydrogenating off-grade Ti sponge, was deoxidized using Mg in a molten magnesium chloride–potassium chloride salt at 933 K under an argon and 20% hydrogen (H_2) mixed gas atmosphere. After deoxidation, the residual Mg-containing salt was separated in situ from the crucible to investigate the feasibility of minimizing salt loss during the leaching and production of pure TiH_2. The results showed that the presence of residual Mg-containing salt inside the crucible strongly influenced whether a mixture of Ti and TiH_2 or pure TiH_2 was produced. When the salt was not sufficiently separated, a mixture of Ti and TiH_2 was obtained and its oxygen (O) concentration was 0.121 mass% under certain conditions. Meanwhile, pure TiH_2 was obtained by increasing the H_2 gas flow rate during deoxidation. Therefore, these results demonstrate that the decrease of O concentration to below 0.180 mass% and the minimal loss of the salt are feasible.

Titanium (Ti) is used in aerospace, biomedical, and chemical processing applications because it and its alloys exhibit excellent properties such as high specific strength, corrosion resistance, and biocompatibility. Accordingly, the demand for Ti, particularly for aerospace applications, continues to increase[1–3]. However, the global production of Ti is lower than that of iron (Fe) and aluminum (Al)[4]. The main reasons for the low production volume of Ti are the low productivity and high processing costs of conventional Ti production processes[5].

In conventional Ti production, the Kroll process, several factors are responsible for its low productivity and high processing cost, such as a batch-type operation and the long processing time[6,7]. Notably, off-grade Ti sponge is generated during the Kroll process[8,9]. It is estimated that 10–20% of the total production volume of Ti sponge[10]. This indicates that the high processing costs can be reduced by developing an efficient utilization method for off-grade Ti sponge. When off-grade Ti sponge can be utilized in Ti ingot production, it not only reduces the high processing costs of Ti but also compensates for the low Ti production volume. In addition, this can decrease carbon dioxide emissions by 95.4% because upgrading low-grade Ti ore and the Kroll process are not required[11]. Therefore, the recycling of off-grade Ti sponge is important.

The main challenge associated with the recycling of off-grade Ti sponge is the removal of major impurities such as oxygen (O) and Fe. These impurities negatively affect the mechanical properties of the final product and are almost impossible to remove from Ti using conventional remelting techniques. As a result, in modern industrial practice, off-grade Ti sponge is cheaply used as an additive in the steel industry. However, when the O concentration in off-grade Ti sponge can be lowered to below 0.180 mass%, which is the American Society for Testing Materials (ASTM) criteria for Grade 1 Ti[12], off-grade Ti sponge can be utilized in Ti alloy production.

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Although Fe cannot be removed directly from off-grade Ti sponge, it can be used as a β-stabilizer in β-Ti alloys[13,14]. Therefore, to recycle off-grade Ti sponge for use in Ti production, a deoxidation process to decrease its O concentration to below 0.180 mass% is necessary.

Numerous methods for deoxidation of Ti using various reducing agents have been proposed. Due to the high affinity of O to Ti, most reducing agents used in the proposed deoxidation processes are limited to rare-earth elements, such as holmium (Ho)[15], yttrium (Y)[16,17], and lanthanum (La)[18], calcium (Ca)[19–29], and electrons[30–32]. However, magnesium (Mg), which is the cheapest among the metallic reducing agents, is not suitable as a reducing agent for deoxidation of Ti. This is because the O concentration in Ti by Mg/magnesium oxide (MgO) equilibrium at 1200 K is approximately 2 mass% in the standard state[33], which is significantly higher than the 0.180 mass%.

In recent years, several studies have been conducted on the deoxidation of Ti using Mg[34–40] to increase its capability to decrease the O concentration in Ti. Some of these studies proposed the promising hydrogen (H) assisted Mg reduction process for the deoxidation of Ti using Mg[34–36], in which the magnesiothermic reduction of Ti is conducted in a hydrogen gas (H_2) atmosphere. In this process, the O concentration in Ti is decreased to 0.0503 mass% when deoxidation is performed at 1023 K for 12 h in an H_2 gas atmosphere[34]. This indicates that the O concentration in Ti can satisfy the ASTM criteria for Grade 1 Ti by the deoxidation even when Mg is used as the reducing agent under a high hydrogen chemical potential.

To develop a novel and efficient recycling process for off-grade Ti sponge, the deoxidation of off-grade Ti sponge using Mg in argon (Ar) and H_2 mixed gas at 933–993 K was investigated by the authors[41,42]. To increase the activity of hydrogen (a_H) in the reaction system and reaction rate, titanium hydride (TiH_2) powder produced by hydrogenating an off-grade Ti sponge was used as the feedstock for deoxidation.

However, several drawbacks remain, such as the loss of residual Mg-containing salts during leaching and the production of a mixture of Ti and TiH_2 instead of pure TiH_2. The production of TiH_2 is preferred to that of Ti, considering the sintering process after the deoxidation process. This is because the sintered compact using TiH_2 powder has a higher sintered density than that using pure Ti powder, which improves the mechanical properties of the final Ti product[43,44]. However, in the authors' previous studies[41,42], a mixture of Ti and TiH_2 was produced after the deoxidation. This was because TiH_2 feedstock inside the salt was dehydrogenated during the deoxidation owing to the low hydrogen partial pressure (p_{H_2}) inside the salt. Therefore, the development of a method for the production of pure TiH_2 is required even after the deoxidation.

In addition, salt loss was unavoidable because the salt was removed during subsequent leaching to recover the deoxidized product. It is worth noting that separating the residual Mg-containing salt from the deoxidized product before leaching can significantly reduce the amount of acid waste solution and the residual Mg-containing salt can be reused for deoxidation. Furthermore, reducing the amount of residual Mg-containing salt to be removed shortens the leaching time; thus, O contamination during leaching can be reduced. Therefore, to simultaneously overcome these drawbacks, the separation of residual Mg-containing salt during deoxidation is necessary.

In this study, a deoxidation process for off-grade Ti sponge was developed with the aim of decreasing the O concentration to below 0.180 mass%, minimizing the loss of residual Mg-containing salt, and producing pure TiH_2. The influence of the reaction time on the O concentration in the residue was investigated. After deoxidation, the feasibility of separating the residual Mg-containing salt was investigated via in situ separation by lifting a wire mesh strainer type of crucible. Furthermore, the influences of the H_2 gas flow rate, hydrogenation temperature, and draining time on the separation of the residual Mg-containing salt and the production of pure TiH_2 were systematically investigated. Figure 1 shows a flowchart of the deoxidation process for off-grade Ti sponge using Mg with a wire mesh strainer type of crucible in an Ar and 20% H_2 mixed gas atmosphere.

Thermodynamic analysis
Deoxidation of Ti using Mg in an Ar and H_2 mixed gas atmosphere
The chemical potential diagram of the Ti–O–H system at 973.15 K was plotted in Fig. 2 using the Chesta software[45] and various thermodynamic data[34,46,47]. The ordinate denotes the oxygen partial pressure (p_{O_2}) and the abscissa denotes the p_{H_2}.

The stability regions of the Ti–O solid solutions are divided by dashed lines depending on the O concentration in Ti (s). The stability region of Ti-0.6 mass% O is located in the p_{O_2} range of 6.5×10^{-54}–8.7×10^{-54} atm and the p_{H_2} range below 5.8×10^{-3}–5.9×10^{-3} atm. The p_{O_2} by the Mg (l)/MgO (s) equilibrium is 6.5×10^{-54} atm at 973.15 K under the standard state. This p_{O_2} is located in the stability region of Ti-0.6 mass% O at p_{H_2} below 5.8×10^{-3} atm. Therefore, when Ti is deoxidized using Mg at p_{O_2} below 5.8×10^{-3} atm under a standard state, the O concentration in Ti will be 0.6 mass%, which is greater than 0.180 mass%. This indicates that the O concentration in Ti cannot be decreased to below 0.180 mass% when Ti is deoxidized using Mg without H_2 gas under standard state.

However, there are two methods to decrease the O concentration in Ti to below 0.180 mass%, even when Mg is used as the reducing agent. One is to decrease the activity of MgO (a_{MgO}). For example, when a_{MgO} is decreased to 0.1, the p_{O_2} by Mg (l)/MgO (s) equilibrium decreases to 6.51×10^{-56} atm, as shown in Fig. 2. This p_{O_2} is located in the stability region of Ti-0.05 mass% O even at p_{H_2} below 5.6×10^{-3} atm. Therefore, although Mg is used as a reducing agent, the O concentration in Ti can be decreased to 0.05 mass% when the removal of the produced MgO during the deoxidation of Ti is maintained via chemical reactions or electrolysis[33,37,38,48].

Another method is utilizing H_2 to deoxidize Ti. As shown in Fig. 2, when p_{O_2} is 6.51×10^{-54} atm determined by Mg (l)/MgO (s) equilibrium at 973.15 K, the stability regions of $TiH_{0.290}O_{0.005}$ (s), $TiH_{0.339}O_{0.005}$ (s), and $TiH_{0.388}O_{0.005}$ (s) are located at p_{O_2} above 5.8×10^{-3} atm, 2.6×10^{-2} atm, and 3.6×10^{-2} atm, respectively. That is, when the p_{H_2} is maintained above 5.8×10^{-3} atm and Mg is used as a reducing agent, the p_{O_2} by Mg (l)/MgO (s) equilibrium is located in the stability regions of $TiH_{0.290}O_{0.005}$ (s), $TiH_{0.339}O_{0.005}$ (s), and $TiH_{0.388}O_{0.005}$ (s) with an O concentration of 0.166 mass%. Although only a few types of TiH_xO_y are plotted owing to the lack of
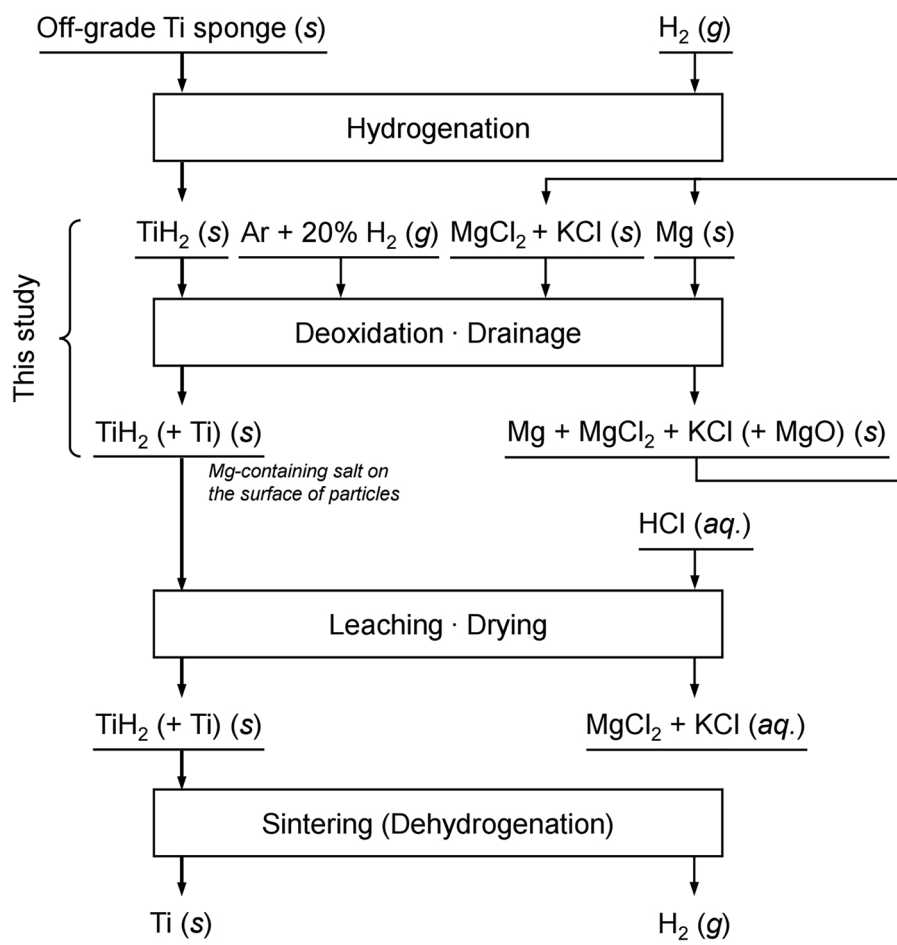
Figure 1. Flowchart of the deoxidation process for off-grade Ti sponge using Mg metal with a wire mesh strainer type of crucible in an Ar and 20% H_2 mixed gas atmosphere.

thermodynamic data[34,47], this diagram demonstrates that the O concentration can be decreased to below 0.180 mass% by deoxidation using Mg when the p_{H_2} is above 5.8×10^{-3} atm even under the standard state.

In this study, Mg was used as the reducing agent. In addition, TiH_2 prepared in advance was used as the feedstock to increase the a_H in the reaction system. As shown in Fig. 1, TiH_2 was produced by hydrogenation of off-grade Ti sponge before deoxidation. Furthermore, to maintain a high p_{H_2} in the reaction system, an Ar and 20% H_2 mixed gas was used during deoxidation and hydrogenation.

TiH_2 production in an Ar and H_2 mixed gas atmosphere

To investigate the feasibility of TiH_2 production, a thermodynamic analysis of the hydrogenation reaction is necessary. The production of TiH_2 by the hydrogenation of Ti with H_2 gas is described by Eq. (1)[46]. In addition, p_{H_2} by Ti (s)/TiH_2 (s) equilibrium can be expressed as shown in Eq. (2) using Eq. (1).

$$Ti\ (s) + H_2(g) = TiH_2\ (s) \tag{1}$$
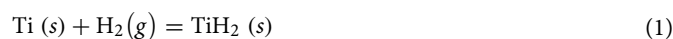
$$\Delta G_r^\circ = -38.6\ \text{kJ} \cdot \text{mol}^{-1}\ \text{at 773 K}$$

$$\Delta G_r^\circ = -10.4\ \text{kJ} \cdot \text{mol}^{-1}\ \text{at 973 K}$$

$$p_{H_2} = \exp\left(\Delta G_r^\circ / RT\right) \tag{2}$$

In Eqs. (1) and (2), p_{H_2}, ΔG_r°, R, and T refer to the H_2 partial pressure (atm), standard Gibbs free energy change for the reaction in Eq. (1) (kJ·mol^{-1}), universal gas constant (kJ·mol^{-1}·K^{-1}), and absolute temperature (K), respectively. As shown in Eq. (2), the p_{H_2} by Ti (s)/TiH_2 (s) equilibrium is a function of the temperature and was calculated to be 2.45×10^{-3} atm, 3.42×10^{-2} atm, and 1.27×10^{-1} atm at 773 K, 873 K, and 933 K, respectively (see Supplementary Fig. S1 online). This result indicates that the production of TiH_2 (s) at 773–933 K in an Ar and 20% H_2 mixed gas atmosphere is feasible.
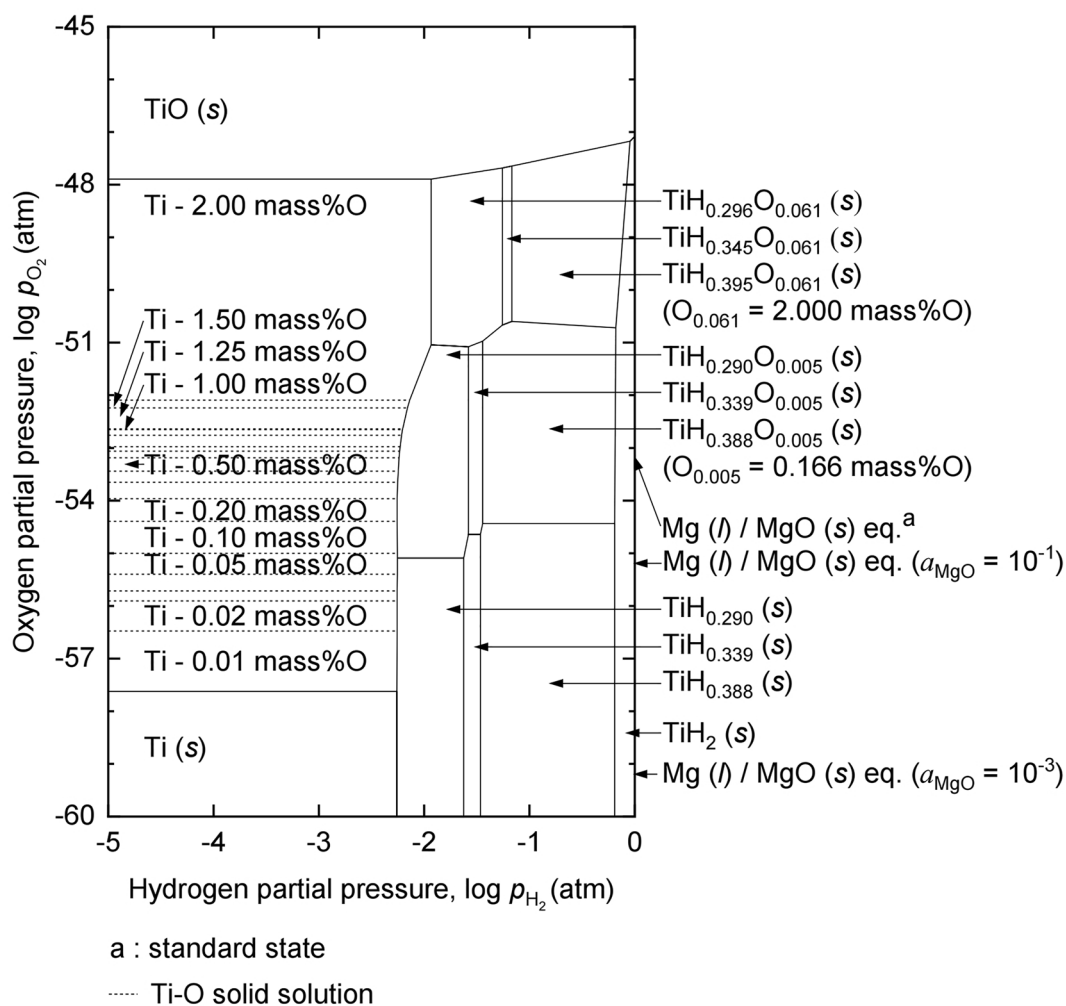
Figure 2. Chemical potential diagram of the Ti-O-H system at 973.15 K.

In the previous study, although the TiH_2 feedstock was deoxidized using Mg in an Ar and 20% H_2 mixed gas atmosphere at 933 K, a mixture of Ti and TiH_2 was produced instead of pure TiH_2[41]. The TiH_2 feedstock was deoxidized in a molten mixture of Mg and magnesium chloride ($MgCl_2$)–potassium chloride (KCl). This indicates that the p_{H_2} inside the molten Mg and salt was low, resulting in the dehydrogenation of TiH_2 during deoxidation. As a result, the production of a mixture of Ti and TiH_2 was unavoidable. It has also been reported that the diffusion of H_2 gas to the Ti sub-hydride (TiH_x with $x < 2$) is impeded when $MgCl_2$ covers the Ti sub-hydride powder[49]. Therefore, to increase the phase ratio of TiH_2 in the mixture of Ti and TiH_2, the p_{H_2} inside the molten salt should be maintained at a high value during deoxidation or the molten salt should be separated during deoxidation enabling to expose of the deoxidized product to a high p_{H_2}.

In this study, a wire mesh strainer type of crucible was used for deoxidation. Deoxidation was performed by lowering the crucible, which contained the TiH_2 feedstock prepared using off-grade Ti sponge, into the molten salt. After deoxidation was finished, the crucible was slightly raised above the surface of the molten salt and maintained for a certain period to separate the molten salt from the crucible and expose the feedstock to a high p_{H_2}.

Methods

Figure 3a shows the schematic of the experimental apparatus used in this study. In addition, Fig. 3b–g show photographs of parts of the Fe crucible assembly and samples used in the experiments. As shown in Fig. 3c, the TiH_2 powder produced from off-grade Ti sponge was used as the feedstock for deoxidation. To prepare the TiH_2 feedstock, off-grade Ti sponge (VSMPO-AVISMA Corporation) was hydrogenated at 973 K for 2 h in an H_2 gas atmosphere at MTIG Co., Ltd. After hydrogenation, the TiH_2 feedstock was pulverized using a mortar and pestle, followed by sieving. The particle size of TiH_2 feedstock used for deoxidation was 150–300 μm.

Before deoxidation, the salt was dried and pre-melted to remove H_2O from the chemical reagents. $MgCl_2$ (anhydrous, purity > 97.0%, Wako Pure Chemical Corporation) and KCl (anhydrous, purity > 99.0%, KOJUNDO Chemical Laboratory Co., Ltd.) were dried at 453 K for 72 h in a vacuum oven (VOS-601SD, EYELA). Subsequently, the dried $MgCl_2$ and KCl were placed inside a reactor, while being contained within an Fe container
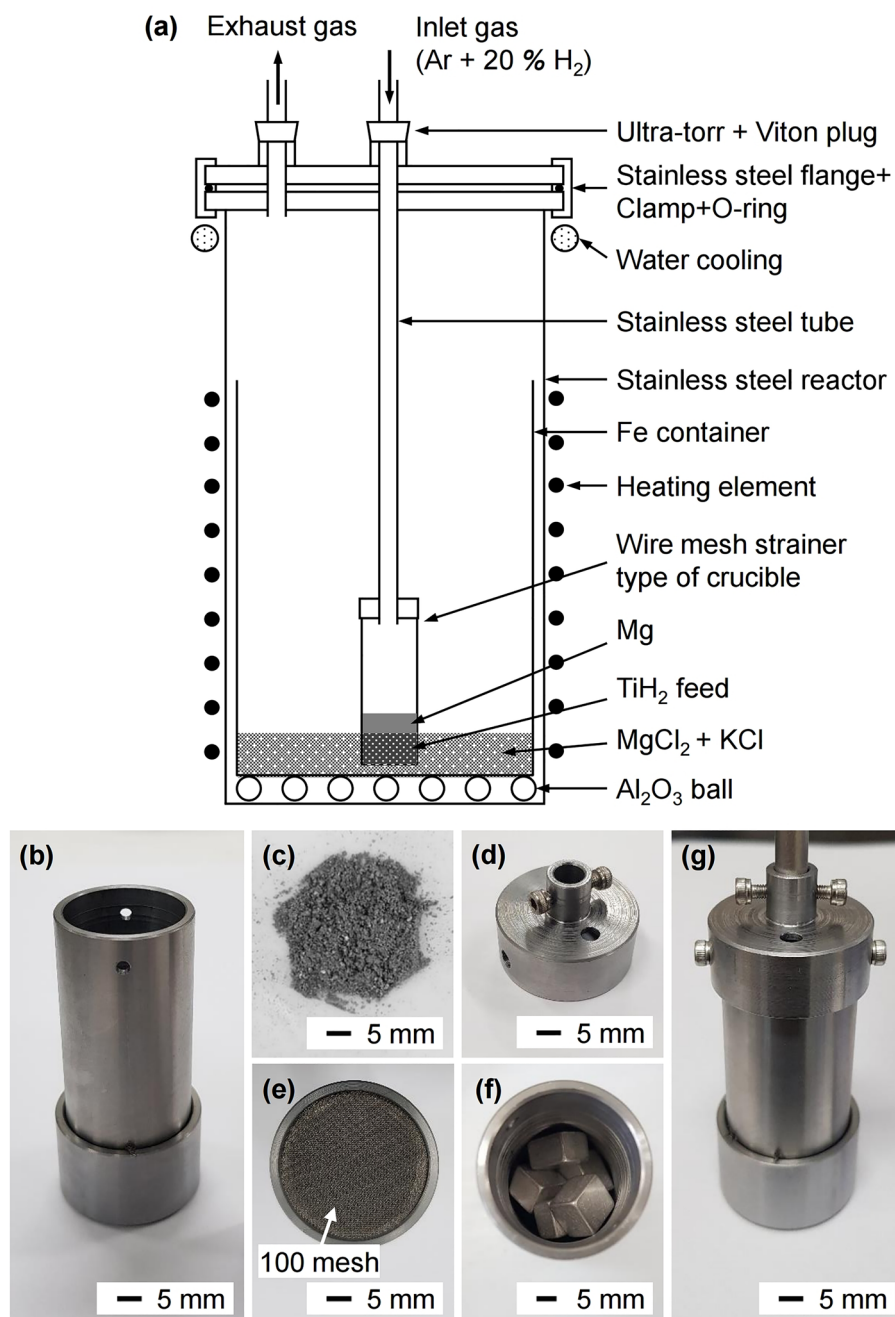
Figure 3. (**a**) Schematic of the experimental apparatus. Photographs of (**b**) the wire mesh strainer type of crucible, (**c**) TiH$_2$ feedstock, (**d**) stainless steel cap, (**e**) Ti mesh (100 mesh) at the bottom of the crucible, (**f**) TiH$_2$ feedstock and Mg inside the crucible, and (**g**) the crucible assembled with the stainless steel cap and tube.

(outer diameter (ϕ) = 89 mm, thickness (t) = 2 mm, height (h) = 200 mm), and pre-melted at 933 K for 2 h in an Ar gas atmosphere.

After the salt was prepared, the TiH$_2$ feedstock and Mg (cubic, width (w) = 10 mm, length (l) = 10 mm, height (h) = 10 mm, purity: 99.99%, RNDKOREA Corporation) were placed in a wire mesh strainer type (Ti mesh, mesh opening size = 100 mesh) of Fe crucible (outer diameter (ϕ) = 29 mm, thickness (t) = 2 mm, height (h) = 70 mm), as shown in Fig. 3f. The crucible was assembled with a stainless steel cap and stainless steel tube, as shown in Fig. 3g. The assembly was set up on the top flange of the reactor and positioned above the Fe container inside the reactor. The top flange and the reactor were fastened, and the reactor was placed in an electric furnace at 298 K.

The interior of the reactor was evacuated for 15 min at 298 K and then filled with an Ar and 20% H$_2$ mixed gas to an internal pressure of 1 atm. The internal pressure of the reactor was maintained at 1 atm until the end of the experiment by constantly flowing mixed gas into the reactor. After controlling the atmosphere, the reactor was heated to 933 K. After 1 h at 933 K, the crucible was immersed in the molten salt by lowering it to 1 mm

above the bottom of the Fe container for deoxidation of the TiH_2 feedstock. After deoxygenation for the duration of 1–24 h, the crucible was lifted to 30 mm above the bottom of the Fe container to be positioned above the molten salt and held for 30 min or 3 h to drain the residual Mg-containing salt from the crucible through the Ti mesh. Subsequently, the crucible was lifted to 329 mm above the bottom of the Fe container, and the reactor was cooled to 298 K.

To hydrogenate deoxidized TiH_2 feedstock, the temperature was held for 24 h after the crucible was lifted to 329 mm above the bottom of the Fe container where the temperature was 773 K, as shown in Fig. 4. In a different manner, after drainage of the residual Mg-containing salt, the crucible was lifted to 269 mm above the bottom of the Fe container where the temperature was 873 K and held for 24 h. The reactor was then cooled to 298 K.

After the experiments, the residual Mg, $MgCl_2$, KCl, and MgO produced inside the crucible were removed by HCl leaching, as shown in Fig. 5. HCl leaching was performed using 1 L of 10% HCl solution at 298 K for 1 h without stirring and by blowing Ar gas into a jacketed reaction vessel. Subsequently, the residues were filtrated and washed with deionized (D.I.) water, followed by washing with acetone. The obtained residues were leached again using 1 L of 10% HCl solution at 298 K for 30 min with stirring at 150 rpm and by blowing Ar gas into a jacketed reaction vessel. After leaching, the residue was filtrated and washed with D.I. water, followed by washing with acetone.

The concentrations of O in the samples were analyzed using an N/O/H determinator (TCH600, LECO Corporation). The crystalline phases of the samples were identified using X-ray diffractometer (XRD: X'Pert MPD, PHILIPS, Cu-Kα radiation).
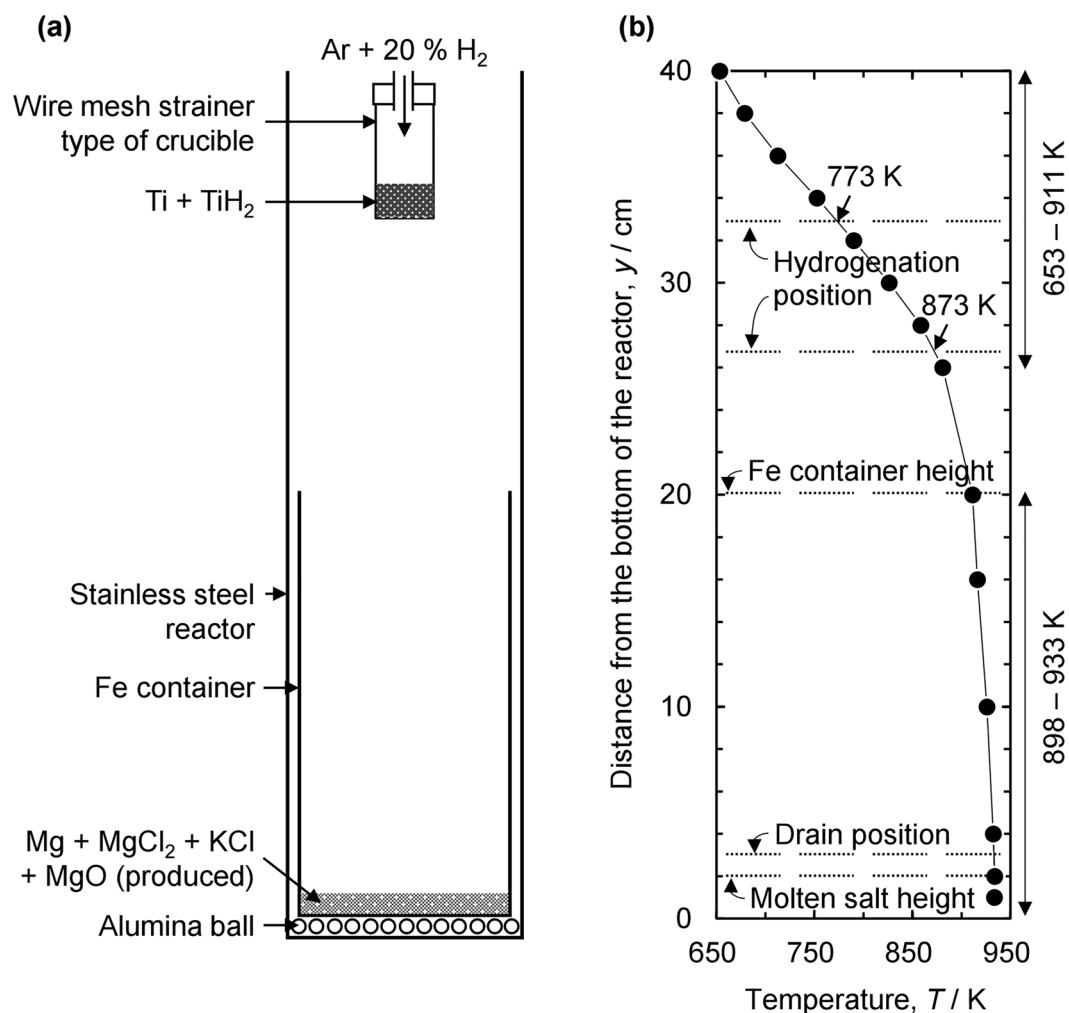

Figure 4. (**a**) Schematic of the interior of the reactor at the hydrogenation step after drainage of the residual Mg-containing salt and (**b**) temperature profile measured along the vertical distance from the bottom of the reactor at 933 K before deoxidation.
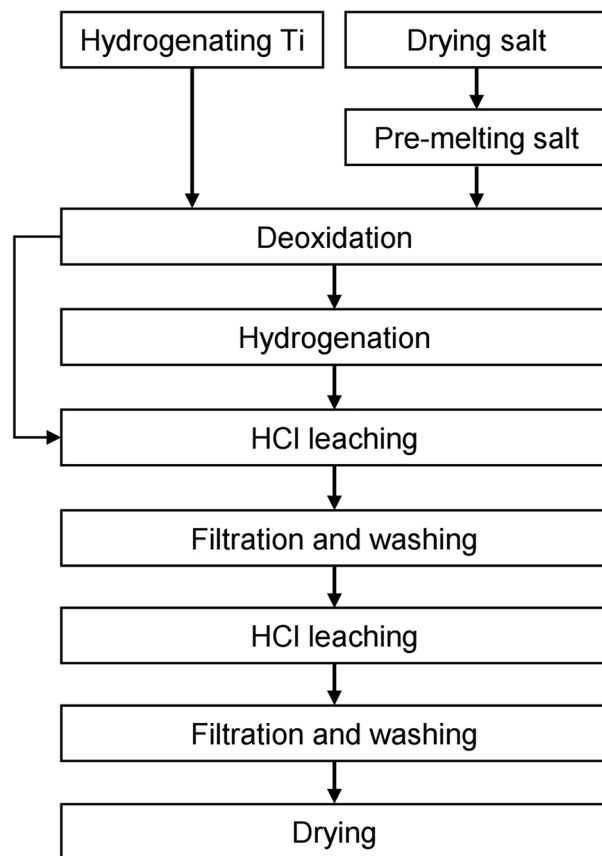
Figure 5. Flowchart of the experimental procedure for the deoxidation of off-grade Ti sponge using Mg metal and the production of TiH_2 powder in an $Ar + 20\%$ H_2 gas atmosphere.

Results and discussion
Deoxidation of TiH₂ feedstock

Figure 6 shows the TiH_2, produced from off-grade Ti sponge by hydrogenation at 973 K for 2 h in an H_2 gas atmosphere according to Eq. (1). The concentration of O in the TiH_2 feedstock was 1.28 mass%, as listed in Table 1.

In addition, Table 1 lists the experimental conditions for the deoxidation of TiH_2 feedstock using Mg in an Ar and 20% H_2 mixed gas atmosphere. In deoxidation, the mass ratios of Mg to feedstock ($r_{Mg/feedstock}$) and salt to feedstock ($r_{salt/feedstock}$) were maintained at 1 and 20, respectively. $r_{salt/feedstock}$ and $r_{Mg/feedstock}$ were calculated using Eqs. (3) and (4), respectively.

$$r_{salt/feedstock} = w_{salt}(g)/w_{TiH_2\_feed}(g) \tag{3}$$

$$r_{Mg/feedstock} = w_{Mg}(g)/w_{TiH_2\_feed}(g) \tag{4}$$

In Eqs. (3) and (4), w_{salt}, $w_{TiH_2\_feed}$, and w_{Mg} refer to the weights of the salt, TiH_2 feedstock, and Mg used, respectively.
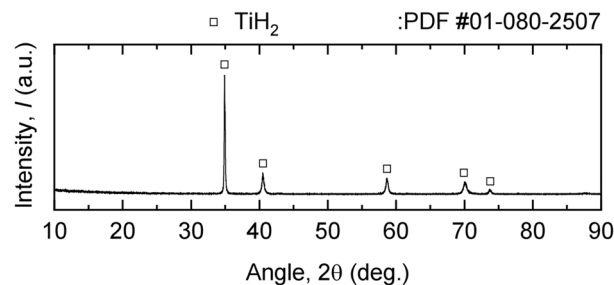

Figure 6. XRD analysis result of the TiH_2 feedstock.

Exp. no.[a]	Time for deoxidation, t_{Deox}/h	Time for hydrogenation, t_{Hydr}/h	Time for draining, t_{Drain}/h	H₂ gas flow rate Deoxidation $f_{H_2,Deox}$/sccm	Hydrogenation $f_{H_2,Hydr}$/sccm	Temperature for hydrogenation, T_{Hydr}/K	Mass fraction of MgCl₂ in MgCl₂–KCl, f_{MgCl_2}[b]	Concentration of O, C_O (mass%)[c]
TiH₂ feed (using off-grade Ti sponge)								1.28
221005	1	–	0.5	300	–	–	0.75	0.218 ± 0.009
221013	3	–	0.5	300	–	–	0.75	0.158 ± 0.008
221019	6	–	0.5	300	–	–	0.75	0.140 ± 0.009
221028	12	–	0.5	300	–	–	0.75	0.132 ± 0.011
221110	24	–	0.5	300	–	–	0.75	0.121 ± 0.013
230105	6	24	3.0	300	300	773	0.55	0.149 ± 0.017
230127	6	24	3.0	300	500	773	0.75	0.154 ± 0.007
230203	6	24	3.0	300	500	873	0.75	0.158 ± 0.002
230111	6	24	3.0	500	500	773	0.75	0.194 ± 0.022

Table 1. Experimental conditions and results of the deoxidation of TiH₂ feedstock. [a]Experimental conditions. 1) Weight of TiH₂ feed, w_{Feed} = 10 g, Total weight of salt, w_{Salt} = 200 g, Weight of Mg, w_{Mg} = 10 g. 2) Temperature for deoxidation, T_{Deox} = 933 K, Atmosphere: Ar + 20% H₂. [b]Mass fraction of MgCl₂ in MgCl₂–KCl was calculated using following equation: weight of MgCl₂/(weight of MgCl₂ + weight of KCl). [c]Determined by N/O/H analysis using TCH600 by LECO corporation.
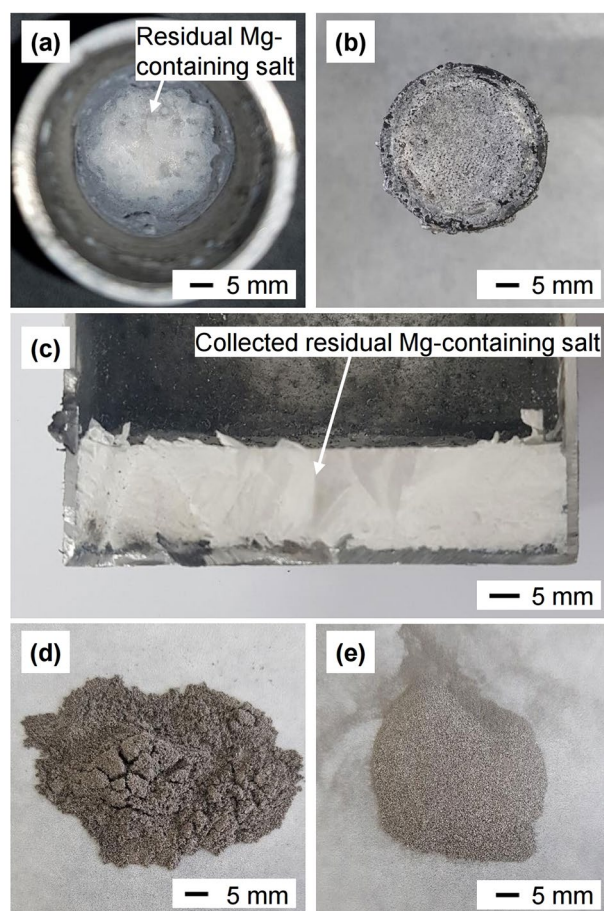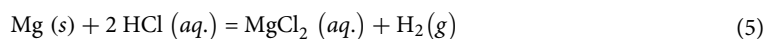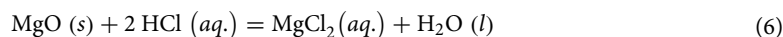

Figure 7. Representative photographs after the experiment: (**a**) residue inside the wire mesh strainer type of crucible, (**b**) residual Mg-containing salt under the Ti mesh at the bottom of the crucible, (**c**) cross-section of the salt collected inside the Fe container, (**d**) residue obtained after the first HCl leaching, and (**e**) residue obtained after the second HCl leaching.

Figure 7a–c show that the residual Mg-containing salt drained through the Ti mesh at the bottom of the crucible when the crucible was lifted to 30 mm above the bottom of the Fe container. The material remaining in the crucible was removed by HCl leaching according to the reactions shown in Eqs. (5) and (6)[50]. After HCl leaching, the deoxidized product was obtained as a fine powder, as shown in Fig. 7d,e.

$$Mg\ (s) + 2\ HCl\ (aq.) = MgCl_2\ (aq.) + H_2(g) \tag{5}$$

$$\Delta G_r^\circ = -463.1\ kJ \cdot mol^{-1}\ at\ 298\ K$$

$$MgO\ (s) + 2\ HCl\ (aq.) = MgCl_2(aq.) + H_2O\ (l) \tag{6}$$

$$\Delta G_r^\circ = -130.9\ kJ \cdot mol^{-1}\ at\ 298\ K$$

As shown in Table 1, the O concentration in the feedstock of 1.28 mass% was decreased with an increasing deoxidation time. As a result, the lowest O concentration was 0.121 mass% when the TiH$_2$ feedstock was deoxidized for 24 h.

As shown in Fig. 2, the equilibrium concentration of O in the deoxidized product was determined by the p_{O_2}, and p_{O_2} was determined by the Mg (l)/MgO (s) equilibrium as a function of the activity of Mg (a_{Mg}) and a_{MgO} in the reaction system. In this study, a_{Mg} was assumed to be unity during deoxidation. This is because, when the $r_{Mg/feedstock}$ was maintained at 1, the amount of Mg used was 51 times larger than the amount required to reduce O in the TiH$_2$ feedstock. The mass ratio of the Mg used to the Mg required was calculated using Eqs. (7)–(9). In addition, a_{MgO} was assumed to be unity because the solubility of MgO in MgCl$_2$ at 1003 K and 1073 K were reported to be only 0.36 mol% and 0.63 mol%, respectively[51–53]. When considering the value of $r_{salt/feedstock}$ and the amount of the MgO produced by complete deoxidation and MgCl$_2$ used, the mol% of MgO in MgCl$_2$ would be 0.51 mol%, which is greater than 0.36 mol%. In addition, the actual mol% of MgO in MgCl$_2$ would be larger than 0.51 mol% when the generation of MgO by reacting MgCl$_2$ with H$_2$O absorbed to MgCl$_2$ owing to its hygroscopic property[54,55]. Moreover, because the MgO solubility in MgCl$_2$ decreases with a decreasing temperature, the MgO solubility in MgCl$_2$ at 933 K is expected to be lower than that in MgCl$_2$ at 1003 K, 0.36 mol%.

$$Mg\ (l) + O\ (s,\ in\ TiH_2\ feedstock) = MgO\ (s) \tag{7}$$
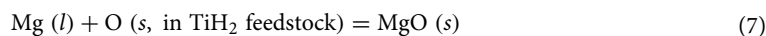
$$w_{Mg\ required} = \left(C_{O,\ in\ the\ feedstock} \times w_{TiH_2\_feed}\ (g)/100\right) \times \left(m_{Mg}/m_O\right) \tag{8}$$

$$r_{Mg\ used/Mg\ required} = w_{Mg}\ (g)/w_{Mg\ required}\ (g) \tag{9}$$

In Eqs. (7)–(9), $w_{Mg\ required}$, $C_{O,\ in\ the\ feedstock}$, $w_{TiH_2\_feed}$, m_O, m_{Mg}, $r_{Mg\ used/Mg\ required}$, and w_{Mg} refer to the calculated weight of Mg to deoxidize O in the TiH$_2$ feedstock, initial O concentration of the feedstock used (mass%), weight of the TiH$_2$ feedstock used (g), atomic mass of O (15.999 g·mol^{-1}), atomic mass of Mg (24.305 g·mol^{-1}), ratio of the amount of Mg used to Mg required, and weight of Mg used (g), respectively.

The thermodynamic analysis results presented in Fig. 2 show that Ti containing O of 0.166 mass% can be obtained under the standard state when the TiH$_2$ is deoxidized using Mg at 973 K under a high hydrogen chemical potential. Although a detailed evaluation of the equilibrium concentration of O in Ti at 933 K was difficult owing to the lack of thermodynamic data, the experimental results, such as the deoxidized product obtained containing O of 0.121 mass%, demonstrated that the experimental results agreed with the thermodynamic analysis results. Consequently, these results show that the O concentration in the off-grade Ti sponge could be decreased to below 0.180 mass% by deoxidizing TiH$_2$ using Mg at 933 K in an Ar and 20% H$_2$ mixed gas atmosphere.

Figure 8 shows the XRD analysis results of the deoxidized product obtained after the experiments. The results showed that the obtained deoxidized product was a mixture of Ti and TiH$_2$. This was because the residual Mg-containing salt was not drained enough to expose the deoxidized product to a high p_{H_2}, as shown in Fig. 7a. When the residual Mg-containing salt was not sufficiently drained, the deoxidized product was covered with the residual Mg-containing salt, placing the deoxidized product at low p_{H_2}. As a result, although high p_{H_2} was maintained in the reaction system using an Ar and 20% H$_2$ mixed gas, the generation of Ti was inevitable. Therefore, to obtain pure TiH$_2$, the residual Mg-containing salt should be sufficiently drained from the crucible after deoxidation.

Production of TiH$_2$ by hydrogenation

To produce pure TiH$_2$ by the hydrogenation of a mixture of Ti and TiH$_2$ obtained after deoxidation, various attempts were made to sufficiently drain the residual Mg-containing salt from the crucible. As shown in Table 1, the H$_2$ gas flow rates for deoxidation and hydrogenation, hydrogenation temperature, and mass fraction of MgCl$_2$ in MgCl$_2$–KCl were varied, whereas the times for deoxidation, hydrogenation, and draining were fixed at 6 h, 24 h, and 3 h, respectively.

Figure 9 shows photographs of the remains inside the crucible after deoxidation, followed by hydrogenation. As shown in Fig. 9a,d, the deoxidized product in powder form was exposed to the atmosphere, unlike the case shown in Fig. 9b,c. These results indicated that the influences of an increase in the H$_2$ gas flow rate during hydrogenation and the hydrogenation temperature on the drainage of the residual Mg-containing salt were insignificant in these experiments, whereas a decrease in the mass fraction of MgCl$_2$ in MgCl$_2$–KCl and an increase in the H$_2$
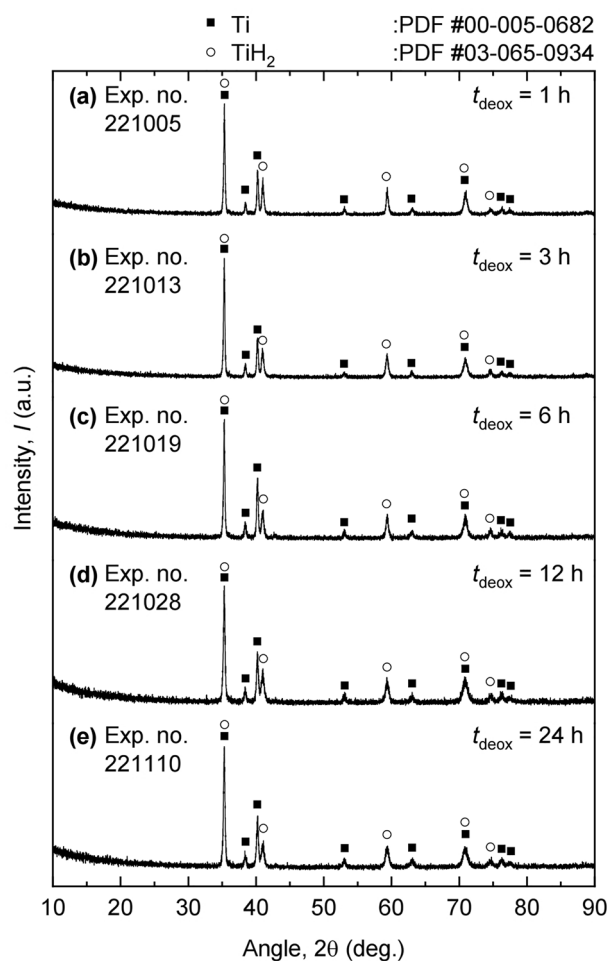
Figure 8. XRD analysis results of the residues obtained after the experiments at the deoxidation times of (**a**) 1 h, (**b**) 3 h, (**c**) 6 h, (**d**) 12 h, and (**e**) 24 h.

gas flow rate during deoxidation enabled further drainage of the salt from the crucible. This was because when the mass fraction of $MgCl_2$ in $MgCl_2$–KCl was decreased from 0.75 to 0.55, the melting point of the molten salt decreased from 844.3 K to 761.2 K (see Supplementary Fig. S2 online)[56]. This allowed the salt to exist as a liquid during hydrogenation at 773 K and to be further drained from the crucible during hydrogenation. In addition, when the H_2 gas flow rate during deoxidation increased from 300 to 500 sccm, the outflow rate of the fluid through the Ti mesh also increased during drainage. Therefore, the residual Mg-containing salt was further drained from the crucible, thereby exposing the deoxidized product to high p_{H_2} atmosphere.

Figure 10 shows the XRD analysis results of the deoxidized product obtained after HCl leaching. As shown in Fig. 10a–c, the obtained deoxidized products were identified as a mixture of Ti and TiH_2. Unfortunately, although the deoxidized product was exposed to the atmosphere when the mass fraction of $MgCl_2$ in $MgCl_2$–KCl was decreased from 0.75 to 0.55, the deoxidized products obtained were identified as a mixture of Ti and TiH_2. This indicated that the residual Mg-containing salt should be more drained from the crucible to produce pure TiH_2. However, Fig. 10d shows that the peak of the Ti phase diminished, and that TiH_2 was identified as the main phase in the obtained deoxidized product. This result indicates that the residual Mg-containing salt was sufficiently drained from the crucible when the H_2 gas flow rate during deoxidation was increased from 300 to 500 sccm. Consequently, the deoxidized product was exposed to high p_{H_2}, which enabled its hydrogenation.

Meanwhile, the O concentrations in the deoxidized products obtained after deoxidation followed by hydrogenation are listed in Table 1. As shown in Table 1, most of the results demonstrate that the O concentration was decreased to below 0.180 mass%. However, when the H_2 gas flow rate was increased from 300 to 500 sccm during deoxidation, the O concentration in the deoxidized product was 0.194 mass%, which is larger than 0.180 mass%. This was attributed to the use of a non-deoxidized Ar and 20% H_2 mixed gas. It is considered that using a purified Ar and 20% H_2 mixed gas is necessary to obtain pure TiH_2 and decrease the O concentration to below 0.180 mass%.

However, the results demonstrated that a decrease in the O concentration to below 0.180 mass% by deoxidation using Mg at high p_{H_2} was feasible, as expected from the thermodynamic analysis. Moreover, it was
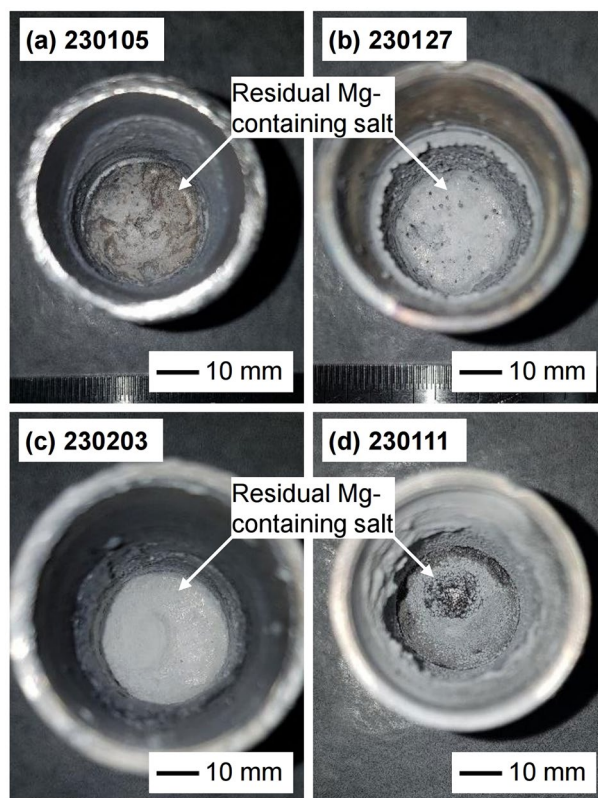
Figure 9. Photographs of the residue inside the wire mesh strainer type of crucible after the experiments using different f_{MgCl_2}, T_{Hydr}, $f_{H_2,Deox}$, and $f_{H_2,Hydr}$ conditions: (**a**) 0.55, 773 K, 300 sccm, 300 sccm; (**b**) 0.75, 773 K, 300 sccm, 500 sccm; (**c**) 0.75, 873 K, 300 sccm, 500 sccm; and (**d**) 0.75, 773 K, 500 sccm, 500 sccm; f_{MgCl_2}, T_{Hydr}, $f_{H_2,Deox}$, and $f_{H_2,Hydr}$ refer to the mass fraction of $MgCl_2$ in $MgCl_2$–KCl, temperature for hydrogenation, H_2 gas flow rate during deoxidation, and H_2 gas flow rate during hydrogenation, respectively.

demonstrated that minimization of the loss of residual Mg-containing salt and the production of pure TiH_2 by utilizing a wire mesh strainer type of crucible during deoxidation were feasible.

Conclusions

The deoxidation process for off-grade Ti sponge using Mg with a wire mesh strainer type of crucible was developed with the aim of decreasing the O concentration to below 0.180 mass%, minimizing the loss of residual Mg-containing salt, and producing pure TiH_2. After deoxidation using Mg in molten $MgCl_2$–KCl salt at 933 K under an Ar and 20% H_2 mixed gas atmosphere for 24 h, the O concentration in the TiH_2 feedstock decreased from 1.28 mass% to 0.121 mass%. This result demonstrates that the O concentration can be efficiently decreased to below 0.180 mass% as expected from the results of the thermodynamic analysis. The production of either a mixture of Ti and TiH_2 or pure TiH_2 was significantly influenced by the drainage of the residual Mg-containing salt from the crucible. As a result, pure TiH_2 was obtained by increasing the H_2 gas flow rate during deoxidation. Therefore, it was demonstrated that the minimal loss of residual Mg-containing salt and the production of pure TiH_2 by the deoxidation process developed in this study were feasible.
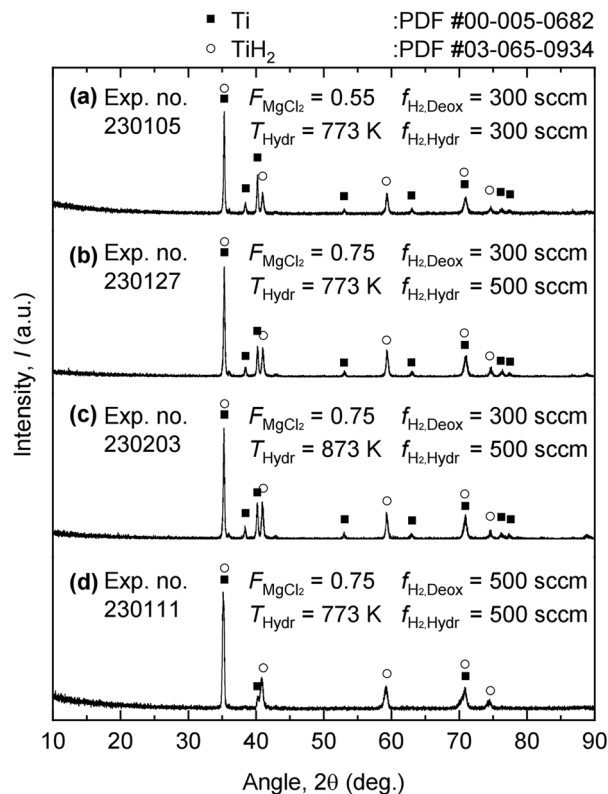
Figure 10. XRD analysis results of the residues obtained after the experiments using different f_{MgCl_2}, T_{Hydr}, $f_{H_2,Deox}$, and $f_{H_2,Hydr}$ conditions: (**a**) 0.55, 773 K, 300 sccm, 300 sccm; (**b**) 0.75, 773 K, 300 sccm, 500 sccm; (**c**) 0.75, 873 K, 300 sccm, 500 sccm; and (**d**) 0.75, 773 K, 500 sccm, 500 sccm; f_{MgCl_2}, T_{Hydr}, $f_{H_2,Deox}$, and $f_{H_2,Hydr}$ refer to the mass fraction of $MgCl_2$ in $MgCl_2$–KCl, temperature for hydrogenation, H_2 gas flow rate during deoxidation, and H_2 gas flow rate during hydrogenation, respectively.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Acknowledgements

Author contributions

This paper and the results were written according to the role of the authors. J.K. was responsible for the overall research and preparation of the research article. S.H.P. wrote the main manuscript and conducted the experiments. H.J.J. was also responsible for the experiments. T.H.L. and H.S.S. were responsible for organizing the data and discussion. All authors reviewed the manuscript.

Funding

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-023-50765-2.

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