CO₂ absorption characteristics of a blanket candidate material Li₂TiO₃ under exposure to different gas mixture

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ABSTRACT

In order to investigate the CO₂ absorption characteristics of the low- and high-density Li₂TiO₃ samples, X-ray diffraction (XRD) and non-Rutherford backscattering spectroscopy (NRBS) analyses have been performed. Crystallographic structure of a sintered sample is decided by the XRD analysis, and the NRBS analysis has evaluated the amount of CO₂ absorption quantitatively. The amount of CO₂ absorption of the low-density Li₂TiO₃ samples is increased with increase of the humidity. We find that the humidity has effect on CO₂ absorption to the low-density Li₂TiO₃ samples. On the other hand, the high-density samples sintered at temperatures higher than 1,470 K absorb very little CO₂ under high humidity conditions.

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1. Introduction

Solid blanket materials of a D-T nuclear fusion reactor should have a role to generate fuel tritium (T). Lithium (Li) compounds with a low chemical activity allowing easy treatment are best fitted for this purpose [1–8]. Especially, Li₂TiO₃ is recommended as the leading candidate among Li compounds, because Li₂TiO₃ has excellent chemical properties such as nonreactivity with H₂O [9] and relatively good T breeding properties among the solid blanket materials with a combination of neutron multipliers such as beryllium for increasing tritium breeding ratio. In this regard, there is an optimum density of Li₂TiO₃. If the Li₂TiO₃ density is too high, the T release rate becomes low due to a decreased permeability. On the other hand, if the density is lowered, the T production rate is decreased [10,11].

Lithium compounds such as Li₄SiO₄ and Li₂ZrO₂ are known as materials absorbing CO₂ at room temperature [12–15]. The carbon contamination of a blanket material should be minimized. It has been reported that C atoms included in a blanket material can form a tritiated hydrocarbon in a T recovery process [16,17]. Therefore, if a blanket material has carbon contamination, the T recovery efficiency would be decreased, because additional process of isotope separation would be required.

In addition, after CO₂ absorption, the surface layers of the Li compounds changes to Li₂CO₃. In the Li₂TiO₃ sample absorbing CO₂, properties necessary as a blanket material such as T release properties, and both thermal and chemical stabilities could be deteriorated, and Li density reduction might occur.

However, the CO₂ absorption properties of Li₂TiO₃ have not yet been studied. In the present paper, we point out that from the CO₂ absorption point of view there is an optimum density of Li₂TiO₃, which is consistent with the optimum determined from the T breeding point of view. In order to investigate the CO₂ absorption properties, we have exposed the Li₂TiO₃ samples with various densities to gases with various compositions; dry CO₂ gas, atmosphere, dry air and moist air. X-ray diffraction (XRD) and non-Rutherford backscattering spectroscopy (NRBS) analyses are carried out to the samples after four case exposures, and crystallographic structure of the exposed samples and the amount of CO₂ absorption are investigated [18,19].

In this work, it is shown that the amount of CO₂ absorbed by the low-density Li₂TiO₃ samples increases with increasing humidity, and that humidity of the exposure gas has a remarkable effect on the CO₂ absorption to the low-density Li₂TiO₃ samples. On the other hand, the amount of CO₂ absorption of the high-density Li₂TiO₃ samples is very little even under high humidity conditions.

2. Experimental

We have prepared the Li₂TiO₃ samples used in the present work by the solid-phase reaction method with Li₂CO₃ (99.9%,
Nacalai Tesque) and the TiO₂ powders (99.9%, Nilaco Co., Ltd.). The Li₂CO₃ and the TiO₂ powders were finely pulverized using an agate mortar and pestle, and were stirred. The mixed powders were compressed and molded for 3 minutes at a pressure of 5 MPa using a press machine.

We have sintered the molded sample at temperatures from 973 K to 1500 K using an electric furnace (As one Co., Ltd.). The sintering conditions for the samples are summarized in Table 1. The low-density Li₂TiO₃ samples were made with sintering for 5 h at temperatures of 973 K – 1000 K. As theoretical mass density of Li₂TiO₃ is 3.43 g/cm³, the ratio of the sample mass density to the theoretical mass density was 0.40, which we call “40% T.D.”.

The medium- and the high-density samples were made by re-sintering the presintered low-density samples as the starting materials. After pulverizing the presintered samples and again molding them, we sintered the samples with densities of 75% T.D.–94% T.D. at temperatures from 1200 K to 1500 K for 5 – 40 h. The sintered samples were disk-shaped with thickness of 2 mm and diameter of 15 mm. We measured the sample mass with a microbalance and the volume with a vernier caliper to calculate the density.

The samples were put in a vacuum chamber evacuated to a pressure of 1 Pa, and were exposed at room temperature to dry CO₂ gas, atmosphere, dry air and moist air at 1 atm. In the case of exposure to moist air, we set a beaker filled with water in the chamber kept at high humidity (> 34,000 ppm). A digital thermohygro meter FL-02 (Tokyo Glass Kikai) was set in the vacuum chamber. The humidity during exposure to dry CO₂ gas and dry air was less than 7000 ppm, while that during exposure to atmosphere was 20,000 – 30,000 ppm.

Samples used in this work were lithium compounds of a Li₂TiO₃. The NRBS analysis is highly sensitive to Li isotopes, and is very effective for blanket material analysis [20]. Placing the sample at the center of the target vacuum chamber, the analyses were performed using 2.6-MeV-proton beams and a silicon surface barrier detector (SSBD) located at 165° with respect to the direction of the beam incidence.

The crystallographic structure of the prepared Li₂TiO₃ samples was investigated by XRD analysis using RINT2000 (Rigaku) with Cu-Kα X-ray at room temperature. The simulation of powder XRD patterns was performed using a Rietveld-analysis program RIETAN [21] and the crystal data for Li₂TiO₃ [22], Li₂CO₃ [23], and TiO₂ [24].

3. Results and discussion

3.1. Low-density Li₂TiO₃ samples under various exposure conditions

XRD analysis was performed on the low-density Li₂TiO₃ samples (41% T.D.) after exposure to dry CO₂ gas in order to investigate crystallographic structure change of Li₂TiO₃. The powder XRD spectra are shown in Fig. 1 in comparison with the as-sintered sample (39% T.D.). The vertical axis is X-ray intensity, and the horizontal axis is the diffraction angle 2θ. Simulation spectra of Li₂TiO₃, Li₂CO₃ and TiO₂ are also shown in this figure. The powder XRD spectral pattern of the as-sintered sample is in good agreement with the simulation spectrum; peaks are observed at 2θ = 19°, 36°, 44°, 48°, 58°, 63° and 67°, which indicates that the sintered samples are converted almost perfectly to Li₂TiO₃. In the spectrum of the low-density Li₂TiO₃ sample after the exposure to CO₂ gas for 2000 h, the XRD peaks of Li₂CO₃ are observed at 2θ = 21°, 31°, and 32°. This clearly indicates that Li₂TiO₃ absorbs CO₂ and then forms Li₂CO₃ and TiO₂ by the dry CO₂ gas exposure.

In XRD spectra of the sample (38% T.D.) exposed to atmosphere for 2000 h, diffraction peaks at 2θ = 19°, 44°, 58° and 63° (Li₂TiO₃), peaks at 21°, 31° and 32° (Li₂CO₃) are observed similarly to the sample exposed to CO₂. The Li₂TiO₃ sample also absorbs CO₂ under long-time exposure to atmosphere, and forms Li₂CO₃ and TiO₂ similarly to the exposure to CO₂ gas.

The ratio of the Li₂CO₃ peak intensity (2θ = 32°) to Li₂TiO₃ peak intensity (2θ = 19°), I₂CO₃/I₂TiO₃, is a quantitative measure for the de-
degree of CO₂ absorption. For the atmospheric and the CO₂ gas exposure sample, the values of I₂/II₉ were almost equal, that is the CO₂ absorption amount were comparable. Since the CO₂ content in atmosphere (only 0.035 vol. %) is overwhelmingly less than CO₂ in the CO₂ gas, the above result means that the atmosphere-exposed sample absorbs CO₂ very selectively.

On the other hand, in XRD spectra of the low-density sample (40%T.D.) exposed to dry air for 2000 h, the Li₂CO₃ peaks (2θ = 21°, 31° and 32°) are observed with much smaller amplitude in addition to the Li₂TiO₃ peaks (2θ = 19° and 44°). Calculating the intensity ratio I₁₉/II₉, we found that the dry air exposure is clearly much less effective than that to CO₂ gas and to atmosphere. The CO₂ concentration in the dry atmosphere is essentially equal to that in the atmosphere. But the amount of Li₂CO₃ produced under dry air exposure is much less than that under atmosphere. In the present work, the humidity of atmosphere is 20,000–30,000 ppm, while that of the dry air is less than 7000 ppm. It is concluded that humidity (water vapor) has a decisive effect on CO₂ absorption.

The exposure to moist air (>34,000 ppm) was also performed on the sample (41%T.D.). After 2000 h exposure, the XRD showed spectra similar to those for samples exposed to CO₂ gas and atmosphere. The intensity ratio I₂/II₉ for the sample with moist air exposure is larger than those under CO₂ gas and atmosphere.

In order to measure the CO₂ absorption amount more quantitatively, the NRBS analysis for the samples before and after the exposure was performed. As a typical example, Fig. 2a shows the NRBS spectrum of the sample (41%T.D.) after moist air exposure for 2000 h compared with that of the sample before exposure. In this figure, the scattered particle yield is plotted as a function of energy. The energies of the scattered particles depend on the target particle mass and the depth at which the target particle is located. As a result, particles scattered by atoms of a specified species form a step-function-like distribution below an energy determined by the mass of the specified atom existing on the surface, which we call “the edge energy”. The edge energy of Ti, O, C and Li is about 2.4, 2.0, 1.8, and 1.4 MeV, respectively. After moist air exposure, a carbon plateau came to appear, and the yield of oxygen increased as compared with the spectrum before exposure. This feature of the NRBS spectrum is common to all other samples after exposure to the CO₂ gas, atmosphere and dry air.

Fig. 2b shows depth distribution of Li, C, O and Ti deduced from the energy spectra. The reason for the apparent non-zero densities in the negative depth region and the finite width of the peak at the surface is a finite energy resolution of the detection system. The spectra are not corrected for the energy resolution. Anyway, integrating the density over the depth from −0.2 to 2.0 μm, we obtain the areal densities of Li, C, O and Ti near the surface layers (<2.0 μm) is as N_Li = 4.3 × 10¹⁰ cm⁻², N_C = 1.4 × 10¹⁰ cm⁻², N_O = 9.8 × 10¹⁸ cm⁻² and N_Ti = 2.2 × 10¹⁸ cm⁻², respectively. The composition ratio of Li/Ti/O:C is then 2.0:10:4.5:0.6. This ratio corresponds to the composition ratio of Li₂TiO₃ (0.6) CO₂.

Fig. 3 shows the dependence of CO₂ absorption amount of the sample exposed to four different gases containing CO₂ as described above. We have performed the NRBS analysis for every 200 h exposure up to 2000 h, and calculated the C areal density N_C in each of the exposure time. The C areal density increases almost linearly in the low exposure range up to about 800 h, beyond which it approaches a saturation value depending on the exposure condition. The saturation values of N_C for exposure under dry CO₂ gas atmosphere, dry air and moist air are 1.0 × 10¹⁸ cm⁻², 1.0 × 10¹⁸ cm⁻², 6.0 × 10¹⁶ cm⁻² and 1.35 × 10¹⁸ cm⁻² respectively. Under CO₂ gas, atmospheric or dry air exposure, the saturation value of the C areal density N_C at saturation was 1.0 × 10¹⁸ cm⁻². Comparing this value with the Ti areal density, we find that 0.5 mol of CO₂ is absorbed in 1 mol of Li₂TiO₃ in the surface region (<2 μm).

Under moist air exposure, N_C at saturation has the maximum. The CO₂ gas and the atmospheric exposure are less effective for the CO₂ uptake. The dry air exposure is further inefficient in this regard. It can be concluded that the amount of CO₂ absorption depends more on the water vapor content than on the CO₂ content itself [25].

Elastic recoil detection analysis (ERDA) was performed to measure hydrogen distributions in the Li₂TiO₃ samples after CO₂ exposure and standard Li₂CO₃ samples. However, change of H concentration in the Li₂TiO₃ and Li₂CO₃ samples was not observed near the surface layers. The water molecules H₂O adsorbed/absorbed on the sample surface might have a function to attract Li ions and promote the CO₂ absorption on the sample surface. The mechanism of the CO₂ uptake is yet to be identified.

3.2. High-density Li₂TiO₃ samples under various exposure conditions

We have performed powder XRD analysis for the high-density Li₂TiO₃ sample (approximately 90%T.D.) after atmospheric, dry air and moist air exposures in order to investigate changes of crystalline structure after exposure. Fig. 4 shows XRD spectra for the high-density samples (88 - 93%T.D.) exposed to atmosphere, dry air and moist air. The exposure time was 2000 h. This figure also shows simulation spectra of Li₂TiO₃, Li₂CO₃ and TiO₂, and spectra of the as-sintered high-density sample.
Fig. 2. (a) The NRBS spectra measured with a 2.6-MeV proton beam for the low-density Li$_2$TiO$_3$ sample (41%T.D.) after exposure to moist air for 2000 h. The NRBS spectra of the as-sintered Li$_2$TiO$_3$ sample are also shown for comparison. (b) Depth distribution of Li, C, O and Ti in the low-density Li$_2$TiO$_3$ sample (41%T.D.) exposed to moist air for 2000 h.

All high-density samples after exposure have Li$_2$TiO$_3$ peaks at $2\theta = 19^\circ$, 44$^\circ$, 58$^\circ$ and 63$^\circ$. On the other hand, the Li$_2$CO$_3$ peaks were not observed. This means that high-density samples (88 - 93%T.D.) did not change their composition after atmospheric and dry air exposures for 2000 h. This is true also for the high-density sample after moist air exposure under which the low-density sample is most likely to absorb CO$_2$.

The FWHM of Li$_2$TiO$_3$ peaks at $2\theta = 19^\circ$, 44$^\circ$ and 58$^\circ$ of the high-density Li$_2$TiO$_3$ XRD spectra is smaller than that of the low-density sample. This means that the grain size of Li$_2$TiO$_3$ is large and the high-density samples sintered at high temperature include many large grains. In other words, vacancies and grain boundaries in the sample are decreased, and the sample density is increased. The samples (88 - 93%T.D.) after exposure to CO$_2$, atmospheric, dry and moist air, we did the NRBS analysis for every 200 h up to 2000 h. Values of C areal density $N_C$ under four exposure conditions of the high-density samples were plotted in Fig. 3. The NRBS spectra are similar to those of the as-sintered sample with no C
Fig. 3. Dependence of the C areal density on time of exposure to dry CO\textsubscript{2} gas, atmosphere, dry air and moist air to the low- and high-density samples.

Fig. 4. XRD patterns of the as-sintered Li\textsubscript{2}TiO\textsubscript{3} sample and changes of XRD patterns after exposure to atmosphere, dry air and moist air for 2000 h in the high-density sample.

Fig. 5. Dependence of C areal density on the atmospheric exposure time for the samples with various densities.
present sample preparation, once we sintered at 1473 K or higher, we cooled the sample by natural heat release. Actually, XRD spectra indicate that the high-density Li$_2$TiO$_3$ samples are very similar to the simulation spectra of monoclinic Li$_2$TiO$_3$, and not to those of cubic one.

The exposures to the ground powder samples sintered at 973 K for 5 h and then at 1473 K for 40 h, and the ground powder sample sintered only at 973 K for 5 h (presintered) were performed. We compared the NRBS spectra of the former sample with those of the latter sample after atmospheric exposure for 400 h. No C peaks / plateau were observed in the NRBS spectra of the former sample. On the other hand, a C plateau and increase in the yield of O were observed in the NRBS spectra of the latter sample. According to the result of our past experiments [ref.], a powder Li$_2$TiO$_3$ sample absorbs more CO$_2$ than a molded sample, and the CO$_2$ absorption rate is also high. From the results, Li$_2$TiO$_3$ sintered at 1473 K or higher absorbs almost no CO$_2$, even if it is ground to micropore to powder Li$_2$TiO$_3$.

Accordingly, the CO$_2$ absorption property of Li$_2$TiO$_3$ largely depends on sample preparing condition, and can be greatly suppressed by sintering at temperatures higher than 1470 K. As mentioned above, while the samples sintered at 1473 K and cooled by natural heat release does not have cubic crystal, the FWHM of the Li$_2$TiO$_3$ peaks in XRD becomes smaller unlike those sintered at low temperature. This tells us that the grains grow, and the sample changes to have highly crystalline structure. The reason why the high-density sample absorb little CO$_2$ can be considered to be the highly crystalline structure grown by sintering at temperatures higher than 1470 K making the sample more dense, which reduces the effective surface area of sample reacting with CO$_2$.

4. Conclusions

The exposures of the low-density Li$_2$TiO$_3$ samples for 2000 h to dry CO$_2$ gas (H$_2$O content is less than 7000 ppm), atmosphere (20,000–30,000 ppm), dry air (less than 7000 ppm) and moist air (more than 34,000 ppm) have been performed. The XRD analysis shows that the low-density Li$_2$TiO$_3$ samples under four different exposure conditions have absorbed CO$_2$, and the composition of a part of the Li$_2$TiO$_3$ samples has changed to a mixture of Li$_2$CO$_3$ and TiO$_2$. The NRBS analysis of the samples shows that C area density absorbed as CO$_2$ by exposures is increased with exposure time. The amount of absorbed CO$_2$ is saturated at exposure time of about 1200 h. The saturated value decreases with decreasing humidity; i.e., in order of moist air, atmosphere, dry CO$_2$ gas and dry air. We have found that Li$_2$TiO$_3$ do not react with H$_2$O, however the humidity is the most important factor affecting the amount of absorbed CO$_2$. Since the low-density Li$_2$TiO$_3$ samples have many vacancies and micro-pores with the small grain size, as the XRD analysis shows for the low-density sample, the effective surface area will be large, and therefore the amount of CO$_2$ absorption is increased. In addition, it is inferred that H$_2$O absorbed on the sample surface might have a function to attract Li ions and promote the CO$_2$ absorption on the sample surface.

On the other hand, Li$_2$CO$_3$ peaks in the XRD spectra are not observed in any case of the high-density sample exposed for long time. The low-density sample most absorbed CO$_2$ under moist air exposure, whereas no C peaks / plateau are observed in the NRBS spectra of the high-density sample after moist air exposure for 2000 h. In the case of Li$_2$TiO$_3$ sintered at high temperatures (higher than 1470 K), as observed with the XRD analysis for the high-density sample, grains grow, and the sample becomes to have highly dense structure, which makes CO$_2$ absorption hard to occur. The situation is similar for other powder samples sintered at high temperatures. This result indicates that a sample with 85%T.D. could be the most suitable one for the blanket materials absorbing little amount of CO$_2$ and breeding reasonable amount of T.

References