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Decomposition of carbon dioxide using mechanically-milled magnetite

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Abstract

In recent years, various studies have been reported on decomposition of carbon dioxide into carbon using iron oxide. This study investigates the ability of mechanically-milled magnetite powder to decompose carbon dioxide as well as the effect of mechanical milling on the crystal structure change. Mechanical milling was performed on magnetite powder using a high-energy vibration ball-milling machine. After 6–12 h of milling, Fe and αFe_2O_3 phases appear in addition to the magnetite phase, followed by disappearance of the αFe_2O_3 phase after 24 h of milling, and an FeO phase appears after 72–168 h. The Fe_3O_4 content phase gradually decreases with milling. The carbon dioxide decomposition with the milled powder was carried out in a quartz tube for 3 h at 773 K. The carbon content of the sample after the CO_2 decomposition increases slightly with the milling time up to 48 h and shows drastic increase when the milling time is longer than 72 h, indicating that the production of FeO phase contributes to the ability of CO_2 decomposition. After the decomposition the sample contains graphite (or other types of carbon), undissolved Fe (both bcc and fcc structure) and Fe_3O_4 phase.

Keywords: Oxide materials; Gas–solid reactions; Mechanical alloying; Phase transitions; X-ray diffraction

1. Introduction

For our future society, reduction of greenhouse effect gases such as carbon dioxide is one of the pressing issues. Various studies on the decomposition of carbon dioxide into carbon using iron oxide have been reported [1–7]. For example, mechanically-milled wustite decomposes CO_2 into C at 573 or 773 K, resulting in the production of magnetite (Fe_3O_4), unlike normal wustite [2].

Phase transformations of iron oxides by ball-milling have been thoroughly investigated over the years [8–14]. According to these reports, it is found that the phase changes of iron oxides depend on the milling atmosphere, the presence of impurities, materials of milling vessel or ball and milling time, etc. Ding et al. reported that almost 100% of FeO phase is produced after 30 h of ball-milling of $Fe + Fe_2O_3$ mixture with the production of Fe_3O_4 as an intermediate product [13], while Sorescu reported that Fe_3O_4 is oxidized to αFe_2O_3 after 70 h of ball-milling [14].

According to the above, if the production of FeO from Fe_3O_4 by the milling is established and it works as “activated” wustite, which can decompose CO_2 into “separable” carbon (not carbide), we can suggest a new carbon fixation system mediated through iron oxides. Thus, the aim of this study is to investigate the phase transformation of Fe_3O_4 and the ability of the produced FeO for carbon dioxide decomposition proposing the new possible system for carbon fixation.

2. Experimental

Fine magnetite (Fe_3O_4) powder (particle size $< 1\ \mu m$) was used as the starting material, in which no impurities or other phases are included, as verified by X-ray analysis. Ten grams of the sample was measured in a glove box under an Ar atmosphere and put in a ball-mill vial with 28 stainless steel balls (3.68 g a piece), with a ball/sample weight ratio of 10/1. The inner pressure of the container was kept constant at 0.2 MPa and no process control agent (PCA) was used. Mechanical milling (12 Hz) was performed up to 168 h using a high-energy vibration ball-milling machine (Supermisni NEV-MA8, Nissin-Giken Co. Ltd., Saitama, Japan). The milled powder was sampled in an Ar atmosphere.

As for CO_2 decomposition experiment, 5 g of the milled sample on an alumina boat was placed in a quartz tube with inner volume estimated at $5.71 \times 10^{-4}\ m^3$ and CO_2 pressure at 0.05 MPa. The tube was heat-treated in a horizontal furnace at 773 K for 180 min. The inner pressure change was monitored at intervals of 5 min.

The carbon content in the powder after CO_2 decomposition was determined using the Carbon/Sulfur Determinator (CS-444, LECO Co. Ltd.). The carbon content measurements by LECO were carried out at least five times. Powder X-ray diffractometry (XRD) with Cu Kα radiation was performed utilizing RINT2000 (Rigaku Co. Ltd., Japan). The 2θ scale was calibrated using the

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internal standard method with silicon powder (99.99% purity, particle diameter < 10 μm).

3. Results and discussion

The X-ray diffraction patterns of the Fe_3O_4 powders are shown in Fig. 1. Before milling, all the X-ray peaks are identified as Fe_3O_4 with inverse spinel type structure. As the milling time is increased, Fe_3O_4 peaks broaden and shift to the lower angle side, indicating an increase of the lattice parameter (0.8394 nm for our unmilled Fe_3O_4 and 0.8406 nm for 48-h-milled Fe_3O_4). The αFe_2O_3 phase with small amount of Fe phase appears after 12 h, and the αFe_2O_3 phase disappears after 48 h. The FeO phase with NaCl type structure, which is more symmetrical than Fe_3O_4 or αFe_2O_3, appears after 72 h and becomes the dominant phase after 168 h. The production of FeO phase is consistent with the results reported by Ding et al. [13] and Sorescu et al. [8], but no description on the milling atmosphere was given in those reports. As a whole, it is found that Fe_3O_4 phase is reduced to FeO and the reductant may be contaminated iron from the stainless vessel. Applying the relation between the non-stoichiometric composition of wustite and the lattice parameter [15], the lattice parameter and x in Fe_xO are determined to be 0.4265 and 0.86 nm, respectively.

On the other hand, when FeO is milled in exactly the same manner, the lattice parameter decreases from 0.4311 nm (0 h) to 0.4276 nm (360 min) with milling time and x decreases from 0.94 to 0.89 nm, respectively [2]. This result may indicate that there is a mechanochemically stable composition at $0.86 < x < 0.89$ for Fe_xO, while thermally stable composition is around $x = 0.946$ [1].

As for the CO_2 decomposition experiments, definite decrease of the inner pressure of the reaction tube is observed for the samples milled for 96 or 168 h, indicating absorption of CO_2.

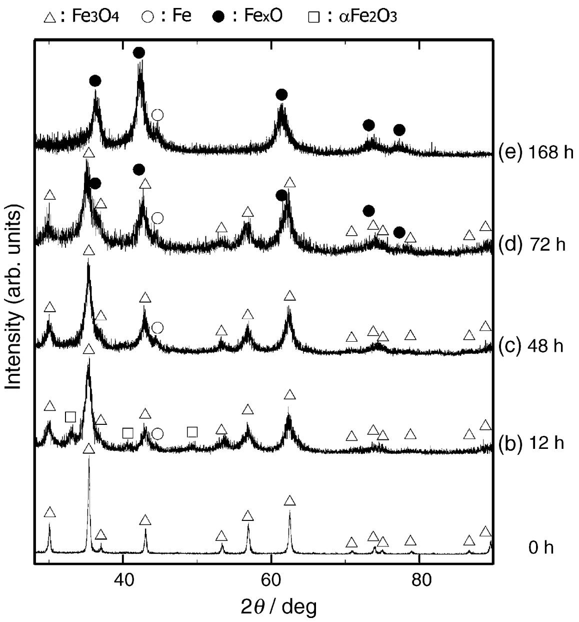

Fig. 1. X-ray diffraction patterns of (a) Fe_3O_4 powder prior to milling process and after (b) 12 h; (c) 48 h; (d) 72 h; and (e) 168 h milling.

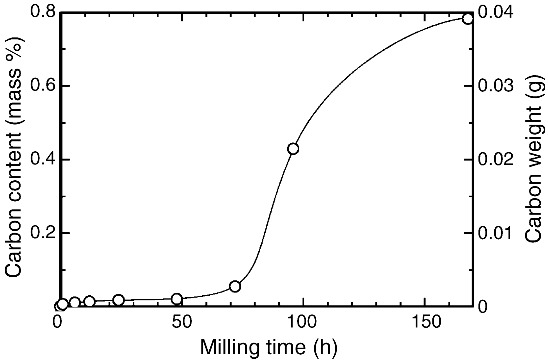

Fig. 2. Carbon contents and weights in the sample after CO_2 decomposition experiments after prior milling.

Fig. 2 shows the carbon content and weight in the samples after the CO_2 decomposition experiments as a function of prior milling time. No trace of carbon is detected for 0-min-milled sample. The carbon content slightly increases with milling time up to 72 h, followed by drastic increase for longer milling times.

In light of the X-ray diffraction pattern (Fig. 1), it is found that the milled Fe_3O_4 contributes to CO_2 decomposition when the milling time is short (1–48 h). Tamaura and Tabata [4] reported that iron-excess magnetite ($Fe_{3.127}O_4$) is produced by annealing Fe_3O_4 in H_2 atmosphere and it decomposes carbon dioxide into carbon at 563 K. Assuming that the similar iron-excess magnetite $Fe_{3+\delta}O_4$ is produced during the milling process in this study, our milled magnetite (48 h) is estimated to be $Fe_{3.052}O_4$ from the relation between δ and the lattice parameter of magnetite [4]. Thus, it is probable that our milled Fe_3O_4 transforms to iron-excess magnetite and works as reductant of carbon dioxide into carbon (or carbon monoxide).

On the other hand, based on the XRD pattern (Fig. 1), the produced FeO seems to play an important role in decomposing carbon dioxide. The higher efficiency for CO_2 decomposition of the milled FeO is consistent with our previous report [2] that the milled FeO decomposes carbon dioxide into carbon and carbon monoxide. Assuming that (i) the amount of other phases is ignored; (ii) non-stoichiometric composition of FeO is ignored; and (iii) both reactions $CO_2 \rightarrow CO$ and $CO_2 \rightarrow C$ proceed during the experiment, it is estimated that the FeO produced from Fe_3O_4 after 168 h milling decomposes 27.8% of the carbon dioxide in the tube into carbon and 23.4% into carbon monoxide. This ability is about 0.4 time lower than that of 60-min-milled FeO and is almost same as that of 5-min-milled FeO [2].

X-ray diffraction patterns of samples pre-milled for 0, 12 and 24–168 h are shown after the CO_2 decomposition in Fig. 3. For all cases, Fe_3O_4 is produced as the major phase after the reaction. The production of small amount of αFe_2O_3 for short milling time indicates the probability that small part of the milled Fe_3O_4 ($Fe_{3+\delta}O_4$) is oxidized to αFe_2O_3. The appearance of Fe phase may be due to the trace of Fe thermally decomposed from $Fe_{3+\delta}O_4$ ($Fe_{3+\delta}O_4 \rightarrow \delta Fe + Fe_3O_4$) or FeO ($FeO \rightarrow Fe + Fe_3O_4$ [2]), or contaminated from SUS vessel.

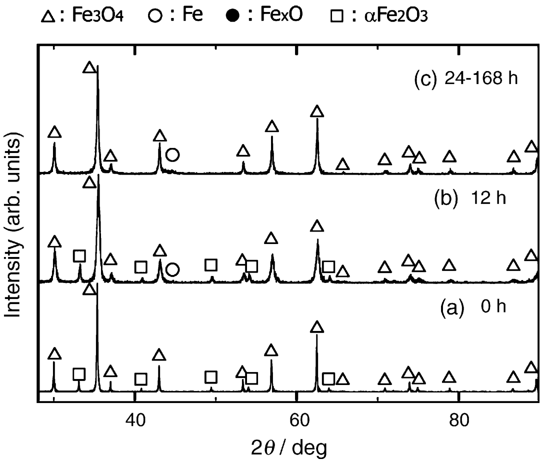

Fig. 3. X-ray diffraction patterns for 0–168 min milled samples after CO_2 decomposition at 773 K.

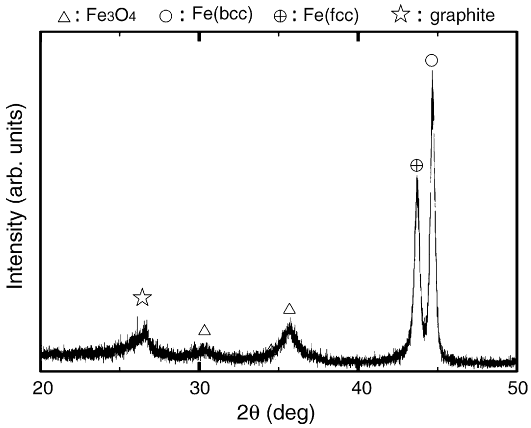

Fig. 4. X-ray diffraction patterns of the undissolved substance after HCl wash of 168-h-milled Fe_3O_4 after CO_2 decomposition.

In order to investigate the nature of the carbon-containing phase (graphite, amorphous or cementite, etc.), the powder sample (168 h milling) after the reaction was dissolved in HCl solution, and the X-ray diffractometry was performed on the undissolved substance (Fig. 4). It appears to be comprised of graphite (or likes of carbon) with undissolved Fe (both bcc and fcc structure) and Fe_3O_4, although it is difficult to identify the phases from a few peaks. It is also interesting to note that not only bcc-Fe but also fcc-Fe phases are identified in the dissolved substance, but, it is not known whether fcc-Fe phase is produced during the milling process or during CO_2 decomposition. The production of carbon and Fe_3O_4 from the produced FeO during carbon dioxide decomposition supports the idea of a new carbon fixation system mediated through iron oxides.

4. Conclusion

The phase transformations of Fe_3O_4 by mechanical milling and the CO_2 decomposition by the milled Fe_3O_4 powders were examined with the following conclusions:

(a) When mechanical milling is performed on Fe_3O_4, Fe and αFe_2O_3 phases appear in addition to the magnetite phase after 6–12 h of milling, followed by disappearance of the αFe_2O_3 phase after 24 h of milling, and appearance of FeO after 72–168 h. The amount Fe_3O_4 phase gradually decreases with milling.

(b) The decomposition of carbon dioxide into carbon slightly increases with milling time when the milling time is within 48 h, for decomposition promoted by the milled Fe_3O_4. On the other hand, for the CO_2 decomposition by the longer milled samples (72–168 h), the FeO produced phase seems to play an important role. After the carbon dioxide decomposition, graphite (or likes of carbon) is included in the sample.

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