Sodium Ferrite/Carbon Dioxide Reactivity for High Temperature Thermochemical Energy Storage

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The reaction of sodium ferrite (NaFeO_2) with carbon dioxide shows great promise for use in new high temperature thermochemical energy storage (TcES) systems. Therefore, the chemical reaction between NaFeO_2 and CO_2 was investigated via thermogravimetric experiments. Analysis of x-ray diffraction patterns confirmed that a mixture of Na_2CO_3 and Fe_2O_3 was completely converted to NaFeO_2 after heating at 900°C . Under a CO_2 pressure of 100 kPa, decarbonation and carbonation of the sample proceeded at temperatures over 850°C and under 750°C , respectively. The starting temperatures of decarbonation and carbonation decreased with decreasing CO_2 pressure. A cyclic experiment was conducted using the pressure swing absorption method at temperatures of 700 – 900°C . The change in reacted mole fraction kept increasing gradually after the second cycle, and it reached 0.835 during the 15th cycle. According to surface observations, a porous structure formed after the 15th cycle. This improved CO_2 diffusivity through the sample and it appears to be the cause of the enhanced reactivity observed during the cyclic experiment with increasing cycle number. The volumetric and the gravimetric thermal energy densities of NaFeO_2 were estimated as 760 kJ L^{-1} and 450 kJ kg^{-1} , respectively. These results indicate that NaFeO_2 has potential to be used as a TcES material at temperatures around 700 – 900°C for utilization of surplus heat in iron-making and other high-temperature processes.

KEY WORDS: thermochemical energy storage; sodium ferrite; carbon dioxide.

1. Introduction

Owing to the mass consumption of energy in the last few decades,¹⁾ the depletion of fossil fuel sources is anticipated. Therefore, the development and introduction of technologies for improving fossil fuel extraction or renewable energy usage have become extremely important research goals.

According to recent studies of energy consumption in Japan,²⁾ over 44% of the energy produced in 2014 was consumed by industry. In particular, the iron and steel industry is one of the most energy intensive sectors and accounted for 32% of industrial energy consumption. Even in countries that are members of the Organization for Economic Co-operation and Development, the iron and steel industry accounted for 10% of total energy consumption in the industrial sector in 2012.³⁾ The quantity of waste heat generated by the iron and steel industry is quite large in China, and 46% of the non-recycled heat represented high temperature thermal energy over 500°C .⁴⁾

Because of this situation, various studies have been conducted to find ways to utilize such waste heat in the iron and steel industry.^{5–8)} Particularly, a suitable thermal energy storage system is essential for an efficient waste heat recovery system, and research into sensible and latent heat storage

has been reported.^{5,6,9,10)} Myagmarjav *et al.*¹¹⁾ proposed a magnesium oxide/water system as a thermochemical energy storage (TcES) system to recover waste heat at a temperature range of 200 – 300°C . Their system had the advantages such as lower energy loss during long-term storage, a high thermal storage density, and a constant temperature output owing to chemical equilibrium. It showed good energy density and demonstrated the potential of TcES systems for applications in the iron and steel industry. Therefore, it can also be expected that TcES systems will be applied for high temperature thermal energy storage in the iron and steel industry. However, so far, only a few carbonation reactions of metallic oxides, such as calcium oxide and lead oxide, have been studied for use in relatively high-temperature TcES systems,^{12–14)} and they have problems with cyclic durability.

In our past reports,^{15,16)} the lithium orthosilicate (Li_4SiO_4)/carbon dioxide (CO_2) system was proposed as a high temperature (700°C) TcES system, and it showed good cyclic durability and potential as a high temperature TcES material. At first, Li_4SiO_4 was developed as a CO_2 separator by Nakagawa and Ohashi.¹⁷⁾ An interesting characteristic is that the reaction temperature between a metallic oxide and CO_2 decreases when the metallic oxide forms a composite oxide with some other material such as Li_2SiO_3 or ZrO_2 .^{17,18)} This can be explained by the Gibbs free energy of reaction, ΔG [kJ mol^{-1}], as shown in Fig. 1.^{19,20)}

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Temperatures at $\Delta G = 0$ are equilibrium reaction temperatures at standard pressure, and decarbonation is thermodynamically favorable above this temperature. The equilibrium temperatures of Eqs. (1) and (2) are 1 600°C and 710°C, respectively, as seen in Fig. 1 and Table 1.

This implies that several series of oxide composites can be developed by changing the combination of a metallic oxide and other appropriate materials, and they have potential to be used in TcES systems.

In order to find a new series of composite oxides, we focused on the sodium ferrite (NaFeO_2)/ CO_2 reaction in this report. NaFeO_2 is a composite oxide of sodium oxide (Na_2O) and iron oxide (Fe_2O_3), and the reaction formulas are described in Eqs. (3) and (4).

According to thermodynamic calculations as shown in Fig. 1, the equilibrium temperature moves from 2 100°C to 1 000°C owing to the addition of Fe_2O_3 . In addition, NaFeO_2 has an attractive price compared with other composite oxides.²¹⁾ Therefore, the $\text{NaFeO}_2/\text{CO}_2$ reaction is expected to be useful as a TcES system at high temperatures. However, few reports of this reaction have been published^{22,23)} to date,

and further investigation is required.

In order to develop NaFeO_2 as a TcES material at high temperatures, the reactivity of a sample at high temperature was measured through thermogravimetric experiments, and its cyclic durability was also investigated. In order to approximate a real TcES system, all experiments were conducted under a 100 vol% CO_2 atmosphere in a closed reactor.

2. Experimental

2.1. Sample Preparation

Sodium carbonate (Na_2CO_3 , 99.98%, Wako Pure Chemical Industries Ltd., melting point: 851°C) and iron oxide (Fe_2O_3 , min. 95.0%, Wako Pure Chemical Industries Ltd., melting point: 1 565°C) were mixed using a mortar and pestle, and then samples were prepared. The molar mixing ratio of $\text{Na}_2\text{CO}_3/\text{Fe}_2\text{O}_3$ was 1:1.

2.2. Thermogravimetric Experiments

All experiments were conducted using a thermobalance (TG-9600S; Ulvac Shinku-Riko Inc.) in a closed system under a 100 vol% CO_2 atmosphere.

Thermal decomposition experiments were conducted with $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ samples. The temperature was increased from room temperature to 900°C at a constant heating rate of 5°C min⁻¹ and kept at 900°C for 30 min. The CO_2 pressure was 100 kPa.

In order to investigate the temperature and pressure dependence of the sample reactivity, thermogravimetric experiments were conducted with $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ samples between 100 and 900°C under various CO_2 pressures (20, 40, 60, 80, and 100 kPa). Samples of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ were heated to remove water at 100°C in advance, and then the CO_2 pressure was controlled at the target values. Subsequently, the temperature was increased to 900°C at a constant heating rate of 5°C min⁻¹. After reaching 900°C, the temperature was decreased to 100°C at a constant cooling rate of 5°C min⁻¹.

The reacted mole fraction, x , was calculated from the mass change of the sample measured by the balance and defined in Eq. (5).

$$x = 1 + \frac{\Delta m / M_{\text{CO}_2}}{m_0 / (M_{\text{Na}_2\text{CO}_3} + M_{\text{Fe}_2\text{O}_3})} \dots\dots\dots (5)$$

Δm [g], M_{CO_2} , $M_{\text{Na}_2\text{CO}_3}$, $M_{\text{Fe}_2\text{O}_3}$ [g mol⁻¹], and m_0 [g] indicate the mass change of the sample, molecular weights of CO_2 , Na_2CO_3 and Fe_2O_3 , and the initial mass of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, respectively.

2.3. Cyclic Experiments

Cyclic experiments were conducted with NaFeO_2 samples using a temperature swing absorption (TS) method under 100 kPa of CO_2 pressure. Initially, $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ samples were heated to remove water at 100°C, and then the CO_2 pressure was held at 100 kPa. Subsequently, the temperature was increased to 900°C at a constant heating rate of 5°C min⁻¹. After that, the temperature varied alternately from 700°C for 1 h as the carbonation process to 900°C for 30 min as the decarbonation process.

Fig. 1. Gibbs free energy changes of metallic oxide/ CO_2 reaction systems.

Table 1. Summary of equilibrium reaction temperatures at standard pressure of metallic oxide/ CO_2 reaction systems.

	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)
Equilibrium reaction temperatures at standard pressure ^{19,20)}	1 600°C	710°C	2 100°C	1 100°C

The changes in reacted mole fraction during the carbonation and decarbonation processes, Δx_{carb} and Δx_{deca} , are expressed by Eqs. (6) and (7), and described in Fig. 2.

$$\Delta x_{\text{carb}} = x_{\text{carb},f} - x_{\text{carb},i} \quad \text{..... (6)}$$

$$\Delta x_{\text{deca}} = x_{\text{carb},i} - x_{\text{carb},f} \quad \text{..... (7)}$$

$x_{\text{carb},i}$, $x_{\text{deca},i}$, $x_{\text{carb},f}$ and $x_{\text{deca},f}$ refer to values of x at the beginning and the end of the carbonation and decarbonation processes in each cycle during the cyclic experiment.

2.4. Characterization

After a $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample was heated at 900°C for 30 min, the sample was characterized by X-ray diffraction (XRD, MiniFlex600, Rigaku).

NaFeO_2 samples after the 1st and 15th cycles during the cyclic experiment were characterized by scanning electron microscopy (SEM, SM-200, Topcon Corp.).

3. Results and Discussion

Figure 3 shows the results of the thermal decomposition of a $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample. Mass loss was observed around 100°C and 850°C . The first drop was completed within 10 min and the mass change was just ~ 1 wt%. The cause for this first drop was presumed to be dehydration of the sample because Na_2CO_3 is hygroscopic and can absorb water easily during handling. On the other hand, the second drop was observed at a temperature of 850°C , completed 10 min after the temperature reached 900°C , and the mass change was around 16.1 wt%. The theoretical mass change due to decarbonation of a $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample is around 16.6 wt%. Therefore, the cause for the second drop in Fig. 3 was considered to be decarbonation of the sample.

Figure 4 shows the XRD pattern obtained from the $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample after heating at 900°C for 30 min. The detected peaks are in good agreement with the literature values for $\alpha\text{-NaFeO}_2$, which are represented by square symbols. Consequently, the sample after the heat treatment is believed to contain a single phase of $\alpha\text{-NaFeO}_2$. This result

also supports the conclusion that the second drop in Fig. 3 was due to decarbonation of the sample.

Figure 5 shows images of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ and NaFeO_2 samples. Both samples were crushed by a mortar and pestle. As shown in Fig. 5(a), the $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample was brown in color owing to the presence of Fe_2O_3 . On the other hand, the NaFeO_2 sample was olive green as shown in Fig. 5(b). Considering that the NaFeO_2 sample contains a single phase of $\alpha\text{-NaFeO}_2$, the cause for this color is presumed to be $\alpha\text{-NaFeO}_2$.

Figure 6 shows the temperature dependence of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample reactivity under 100 kPa of CO_2 . Decarbonation of the sample was first observed at a temperature around 850°C , and it proceeded almost completely when the temperature reached 900°C . At this time, the reacted mole fraction was 0.02. During the cooling process, carbonation of the sample was observed when the temperature reached about 750°C . It proceeded until the temperature reached approximately 550°C , and the reacted mole fraction was ~ 0.73 . This result confirms that a NaFeO_2 sample can react with CO_2 around 800°C and can therefore potentially be used as TcES material.

In order to investigate the dependence of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$

Fig. 3. Thermal decomposition of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample.

Fig. 2. Definition of changes in reacted mole fraction during carbonation and decarbonation processes.

Fig. 4. XRD patterns of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sample after heating at 900°C .

Fig. 5. Images of (a) $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ and (b) NaFeO_2 powders.

Fig. 7. Pressure dependence of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ reactivity during (a) heating and (b) cooling processes.

Fig. 6. Temperature dependence of $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ reactivity under 100 kPa of CO_2 pressure.

reactivity on pressure, the same thermogravimetric experiments were conducted under 5 different CO_2 pressures. Results are shown in Fig. 7, where the reacted mole fraction is plotted as the vertical axis and temperature during the heating and cooling processes as the horizontal axis. During the heating process, as shown in Fig. 7(a), decarbonation was observed under all CO_2 conditions. The temperatures at which decarbonation began were around 760, 800, 820,

840, and 860°C when the CO_2 pressures were 20, 40, 60, 80, and 100 kPa, respectively. Reacted mole fractions reached 4–7% at 900°C. Figure 7(b) shows the pressure dependence of sample reactivity during the cooling process. Carbonation was observed under all CO_2 conditions, although it proceeded more slowly under a pressure of 20 kPa. The temperatures at which carbonation started were around 640, 680, 730 and 750°C when the CO_2 pressures were 40, 60, 80, and 100 kPa, respectively. The highest reacted mole fraction was 0.78 under 80 kPa at 400°C. These results confirm that carbonation/decarbonation of NaFeO_2 proceeds around 800°C, and operating conditions can be obtained from Fig. 7.

Figure 8 shows the result of a cyclic experiment using NaFeO_2 . Carbonation and decarbonation proceeded at 700°C for 1 h and at 900°C for 30 min under 100 kPa of CO_2 pressure, respectively. As shown in Fig. 8, Δx_{carb} and Δx_{deca} were 0.714 and 0.743 in the first cycle, respectively. They decreased slightly in the second cycle, and then they continued increasing gradually after the second cycle. Finally, Δx_{carb} and Δx_{deca} reached 0.835 and 0.839 on the 15th cycle, respectively. This result indicates that NaFeO_2 has sufficient cyclic durability at high temperatures.

Figure 9 shows SEM images of NaFeO_2 samples before and after carbonation and after 15 cycles under 100 kPa of CO_2 pressure. As shown in Figs. 9(a)–9(c), small particles (around 1 μm) of NaFeO_2 are mutually connected to each

other and form aggregates. After carbonation, the small particles have almost disappeared, and the spaces between particles have clearly decreased in Figs. 9(d)–9(f). This seems to have occurred due to carbonation and sintering at high temperature, and this seemingly caused the decrease in reactivity during the 2nd cycle in Fig. 8. On the other hand, the porous structure of the sample appeared after the

15th cycle as shown in Figs. 9(g)–9(i). It seems that CO_2 diffusivity was enhanced due to the porous structure, and this appears to be the cause of the reactivity enhancement during the cycle experiment corresponding to increasing cycle numbers as shown in Fig. 8.

The volumetric thermal energy density, q_v [kJ L^{-1}], of NaFeO_2 can be calculated using Eq. (8).

$$q_v = \frac{-\Delta H_r \rho_a \Delta x_{\text{carb}}}{2 * M_{\text{NaFeO}_2}} \quad \text{..... (8)}$$

ΔH_r [kJ mol^{-1}], ρ_a [kg L^{-1}], Δx_{carb} [–], and M_{NaFeO_2} [kg mol^{-1}] indicate the reaction enthalpy change, the apparent density of the NaFeO_2 sample, the change in the reacted mole fraction, and the molecular mass of NaFeO_2 , respectively. ΔH_r was calculated at 700°C using a commercial software package¹⁹⁾ and found to be -119 kJ mol^{-1} . The apparent density, ρ_a , was measured by a gravimetric method and found to be 1.70 kg L^{-1} . The molecular mass, M_{NaFeO_2} , is 111 g mol^{-1} and q_v was estimated to be 760 kJ L^{-1} . Finally, the gravimetric thermal energy density of NaFeO_2 , q_g [kJ kg^{-1}], can be calculated using Eq. (9), and it was estimated to be 450 kJ kg^{-1} . These results indicate that NaFeO_2 has the potential to be used as a TcES material around 700 – 900°C for the utilization of surplus heat in iron-making and other high-temperature processes.

$$q_g = \frac{-\Delta H_r \Delta x_{\text{carb}}}{2 * M_{\text{NaFeO}_2}} \quad \text{..... (9)}$$

Fig. 8. Cyclic durability of NaFeO_2 reactivity under 100 kPa by TS method. Carbonation process: 700°C for 1 h. Decarbonation process: 900°C for 30 min.

Fig. 9. SEM images of (a–c) NaFeO_2 sample (d–f) after carbonation, and (g–i) after 15 cycle under 100 kPa as CO_2 pressure.

4. Conclusion

Thermogravimetric experiments were conducted with the aim of investigating the reaction between NaFeO_2 and CO_2 . XRD analysis confirmed that $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ samples were converted into NaFeO_2 after heating at 900°C . Decarbonation and carbonation reactions proceeded at temperatures above 850°C and below 750°C under 100 kPa of CO_2 pressure, respectively. The starting temperatures for decarbonation and carbonation decreased with decreasing CO_2 pressure. A cyclic experiment was conducted using a pressure swing absorption method at $700\text{--}900^\circ\text{C}$. The change in the reacted mole fraction kept increasing overall after the second cycle, and it reached 0.835 during the 15th cycle. From the results of SEM imaging, a porous structure was formed after the 15th cycle. This improved CO_2 diffusivity appears to be the cause of enhanced reactivity with increasing cycle number during the cyclic experiment. The volumetric and the gravimetric thermal energy densities of NaFeO_2 were estimated as 760 kJ L^{-1} and 450 kJ kg^{-1} . These results indicate that NaFeO_2 has the potential to be used as a TcES material around $700\text{--}900^\circ\text{C}$ for utilization of surplus heat in iron-making and other high-temperature processes.

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