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Durability characteristics of the hydration of magnesium oxide under repetitive reaction

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The durability of the magnesium oxide/water reaction system under repetitive reaction conditions was examined experimentally to demonstrate the operability of a magnesium oxide/water chemical heat pump. Changes in the reactivity in the hydration of magnesium oxide, which was the most sensitive process in the repetitive reaction, were measured at hydration temperatures from 90–170 °C and pressures from 31.2–70.1 kPa. A lower temperature and a higher pressure for the hydration reaction were effective in maintaining reactivity. The effect of different reaction conditions experienced during repetitive cycles to the standard repetitive cycle was discussed. From microscopic observations, nucleation in primary particles of the material induced by the structure change during repetitive reaction was an important factor in the enhancement of durability. *© 1999 Kluwer Academic Publishers*

Nomenclature

C_V	bulk concentration of vapor [kg/m^3]
D_V	effective diffusivity of vapor [m^2/s]
ΔH°	enthalpy change of reaction [kJ/mol]
M	molecular weight [g/mol]
P	pressure [Pa]
r	radius of the particle [m]
T	temperature [°C]
t	hydration time [s]
t^*	characteristic time [s]
w_{MgO}	magnesium weight in the sample [g]
Δw_{H_2O}	weight change of sample due to reaction [g]
x	reacted fraction [mol %]
Δx_{at}	extent of hydration attained after 60 min of the reaction [mol %]
Δx_h	reacted fraction amount of the hydration [mol %]
η	ratio index [-]
ρ	density of solid reactant [kg/m^3]

Subscripts

h	hydration
H_2O	water
MgO	magnesium oxide
sd,f	saturated reacted fraction of the dehydration of magnesium hydroxide at the former dehydration cycle

1. Introduction

A chemical heat pump using a reversible magnesium oxide/water reaction system has been examined by Kato *et al.* [1] to promote thermal energy utilization. The heat pump examined in this study is based on the following equilibria:

$$\mathrm{MgO\ (s) + H_2O\ (g) = Mg(OH)_2\ (s)}, \quad \Delta H_1^\circ = -81.02\ \mathrm{kJ/mol} \tag{1}$$

$$\mathrm{H_2O\ (g) = H_2O\ (l)}, \qquad \Delta H_2^\circ = -40.02\ \mathrm{kJ/mol} \tag{2}$$

This heat pump makes it possible to store thermal energy by the dehydration of magnesium hydroxide ($Mg(OH)_2$) of Equation 1, and release this on demand by the hydration of magnesium oxide (MgO). A previous study showed that the heat pump could be used as a heat amplifier to transform a heat source at 70–90 °C to one at 100–150 °C, storing the heat at a temperature of 350 °C [2]. The pump is also expected to contribute to load leveling in electrical power generation systems by storing surplus electricity generated during the night as heat energy and resupplying it to users during peak-demand periods. The heat pump is effective for co-generation of energy also, by utilizing heat in the exhaust gas of the system's diesel or gas engine.

Previous studies using a thermobalance showed that the hydration of magnesium oxide controlled the overall rate of heat pump operation [1]. Heat pump operation was demonstrated using a laboratory-scale heat pump with a reactor bed containing 1.8 kg of reactant [3]. The pump had an output of up to 100 W/kg.

One cycle of operation comprises both the hydration and dehydration of MgO. For practical utilization of the heat pump, more than 100 repetitions of the cycle are required. Therefore, the reaction material chosen for the heat pump must be capable of enduring repetitive reaction. However, the reaction material used to date, common $Mg(OH)_2$, is not durable enough, and loses half of its reactivity during the first 10 repetitions.

Different kinds of magnesium oxide materials have been tested in a previous study [4]. A new magnesium oxide material using ultra fine magnesium oxide powder as the precursor was the most appropriate material for the heat pump, because it exhibited high durability and high heat output performance compared to the other oxides. Although reactivity of the new material decreased during the initial five reaction cycles, the reactivity remained relatively constant over the next 19 cycles. Thus, comprehensive durability of the new material for the repetitive reaction was demonstrated in this work. In particular, the hydration of magnesium oxide that is the most sensitive to the repetition was demonstrated. This reaction corresponds to the heat output process of the heat pump. The dependence of the repetitive reactivity on hydration temperature and pressure was examined experimentally. The effect of changes in the reaction conditions on the repetitive durability was also discussed from the standpoint of the practical operation of the heat pump. The durability characteristics of the reaction were related to these measurements and microscopic observations.

2. Experiments

2.1. Reaction materials

$Mg(OH)_2$ material using ultra fine magnesium oxide powder as the precursor was chosen for the experiment. Two grams of ultra fine magnesium oxide powder (avg. particle diameter: 10 nm; UBE Co. Ltd.) was packed in a ball mill with 50 g of purified water and alumina balls. The hydration of MgO was achieved by rolling the mill for 20 hours. After hydration, the pasty product was dried at 80 °C for 24 h, and the resulting flakes were sieved. Particles having average diameter of 1 mm were used for the following experiments.

2.2. Repetitive reaction experiments

The reactions were studied using a thermobalance under a flow system. A 15 mg material sample placed in a platinum cell was installed in the reactor of a thermobalance (TGD-9600, Shinku-riko Co. Ltd.). The temperature at the bottom of the cell, which was considered to be the reaction temperature, was controlled by an electric furnace and directly measured by a thermocouple. Each repetitive experiment was proceeded as following sequence.

$$\begin{array}{ccccccccc} & \text{Original Dehydration} & & \text{Hydration} & & \text{Dehydration} & & \text{Repetition} & \\ Mg(OH)_2 & \longrightarrow & MgO & \longrightarrow & Mg(OH)_2 & \longrightarrow & MgO & \longrightarrow & \ldots \\ \multicolumn{5}{l}{|\text{———— 1st cycle ————}||} & \multicolumn{4}{l}{\text{———— 2nd cycle ————}\ldots} \end{array} \qquad (3)$$

Since the hydration is most influential to the reaction condition, and controls the whole heat pump operation rate, the hydration reactivity is mainly discussed in this study.

The initial sample was in hydroxide form, and contained water physically adsorbed at atmospheric temperature. During the initial dehydration of $Mg(OH)_2$, the physically adsorbed water was removed in a 100 ml/min flow of dry nitrogen gas at 110 °C for 30 min. After this procedure, the reaction temperature was raised at a rate of 50 °C/min up to 350 °C and $Mg(OH)_2$ was dehydrated at this temperature (T_d) for 60 min. The samples had changed to a MgO state. In all subsequent cycles, the dehydration was repeated under the same reaction conditions, save for the initial removal procedure for the physically adsorbed water.

In the hydration experiment, a mixture of purified water vapor and nitrogen carrier gas was supplied to the reactor. The hydration pressure (P_h) was set by the proportion of vapor in the reaction gas. After cooling the reactor to the desired hydration temperature (T_h) in a nitrogen atmosphere, hydration of MgO was achieved under hydration pressure. Several hydration conditions were examined in the repetitive tests. The hydration temperatures were from 90 to 170 °C, which corresponded to the heat output temperature of the heat pump operation. The hydration pressures were 31.2, 47.4, 57.8 and 70.1 kPa, which corresponded to saturated vapor pressures at temperatures of 70, 80, 85 and 90 °C, respectively. These temperatures corresponded to that of a low-temperature heat source for the heat pump in its heat output mode.

The reacted fraction could be calculated by measurement of the sample weight change. It was concluded that the sample's weight change during the reaction was due to the movement of water. Therefore, the reacted fractin, x [mol %], was defined as follows

$$x = 100 \bullet \left(1 + \frac{\Delta w_{H_2O}/M_{H_2O}}{w_{MgO}/M_{MgO}}\right) \qquad (4)$$

where w_{MgO} and Δw_{H_2O} are the weight of magnesium oxide in the sample, and the weight change of the sample caused by the reaction, respectively. The initial state samples contained physically adsorbed water. Thus, the state after the physically adsorbed water was removed was defined as a fraction of 100 mol %. The hydration experiments started from the dehydrated sample state. However, dehydration of each sample did not proceed to $x = 0$ mol %, and the sample saturated at about $x = 10$ mol % [Kato *et al.*, 1998]. In order to obtain an objective comparison of the hydration of the materials, the reacted fraction amount, Δx_h [mol %], is defined as follows.

$$\Delta x_h = x_h - x_{sd,f} \qquad (5)$$

where x_h and $x_{sd,f}$ are the reacted fraction of hydration, and the saturated reacted fraction of the former dehydration cycle, respectively.

The durability characteristics of the hydration were considered in the experiment from the standpoint of practical heat pump operation. To investigate the dependency of the repetitive durability on the reaction conditions, the repetitive reaction was measured under fixed conditions at the hydration temperature of 90–150 °C and pressure of 31.2–57.8 kPa. The effect of different reaction conditions experienced during the repetitive cycle was also examined under some conditions of the temperatures of 90–170 °C and pressures of 31.2–70.1 kPa, because the practical heat pump operation was accompanied with various reaction condition changes. To clarify the fine structure change of the material during the repetition, samples of materials which had experienced the repetition were examined by using a transmission electron microscope (TEM).

3. Results

3.1. Durability under fixed conditions of repetitive reaction

Fig. 1a shows the reactivity change over twelve cycles of repetitive reaction under fixed hydration conditions, temperature (T_h) of 90 °C and vapor pressure (P_h) of 47.4 kPa. The graph shows that the reactivity decreases during the initial four repetitions, but remains constant at about 50 mol % from the 5th cycle to the 12th repetition. Later cycles have a higher activity compared to that of the 4th or 7th cycle. Fig. 1b shows the result under a higher hydration temperature of 130 °C. The initial reactivity decrease is more marked than under the condition of Fig. 1a. On the other hand, after this initial decrease, the reactivity remains roughly constant from the 5th cycle to the 12th. An objective indication of reactivity, the Δx_h attained after 60 min of each cycle of the hydration, is defined as an extent of hydration attained, Δx_{at}. The changes of Δx_{at} during repetitive cycling are shown under some hydration conditions in Fig. 2. Fig. 2a shows the effect of the hydration temperature on the repetitive reactivity. The hydration reactivity decreases during the initial cycles and becomes roughly constant at the following cycles. At the lower hydration temperature of 90, 105 and 110 °C, the initial reactivity decreases are observed during the initial three or four cycles, and the following cycles have constant reactivity. The higher the temperature, the more cycles are required to reach constant reactivity. The extent of hydration attained at 130 or 150 °C decreases compared with that of the lower temperature results. At lower temperatures of 90 and 105 °C, some recovery of the extent of hydration attained is observed. Fig. 2b shows the effect of the hydration pressure on the repetitive reactivity. The higher the reaction pressure rises, the larger the extent of hydration attained becomes, and the smaller the repetition time for the initial reactivity decrease. At the highest pressure, some recovery of the extent of hydration attained is obtained after six cycles.

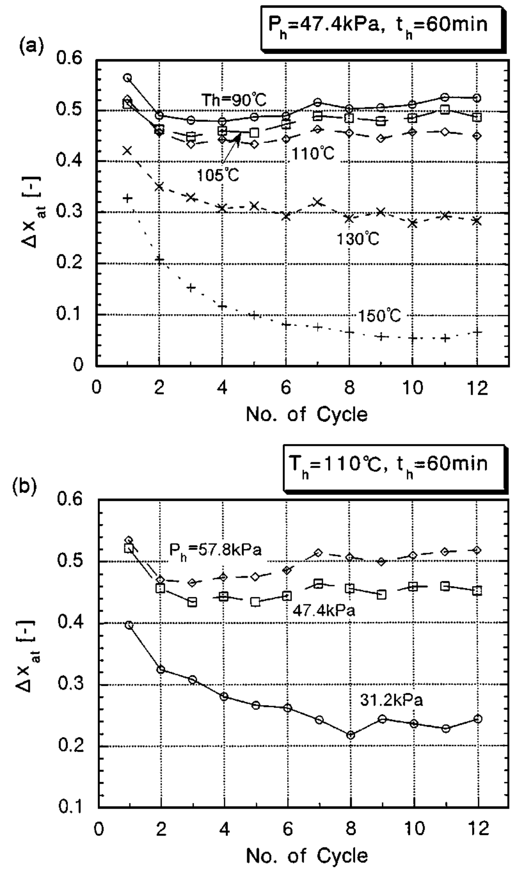

Figure 2 Change of the extent of hydration attained, Δx_{at}, during repetitive reaction; (a) effect of the hydration temperature and number of cycles on the value, (b) effect of the hydration pressure.

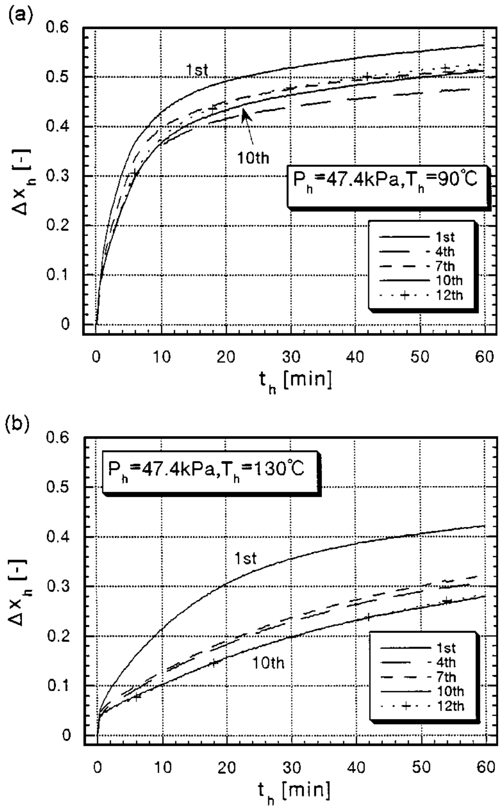

Figure 1 Reactivity change during repetitive reaction; (a) under high durability conditions, (b) under low durability conditions.

3.2. Effect of change in reaction conditions on the repetitive durability

The effect of change in hydration conditions on the repetitive durability was examined in the three types of experiments; that is, the effect of high-temperature hydration, low-temperature hydration and multiple hydration conditions on the durability. Fig. 3a shows the effect of some high-temperature hydration cycles on the repetition. After stable reactivity was attained (at 7 cycles repetition) at the low hydration temperature of 110 °C, the sample was subjected to high-temperature hydration cycles of 130, 150 and 170 °C. Subsequently, the sample was hydrated at 110 °C in the 11th cycle. The last cycle of low-temperature repetition was not affected by the high-temperature hydration cycle, and the extent of hydration recovered to its former value before the 7th cycle, i.e. the reactivity of the low-temperature hydration was maintained after a high-temperature experience. Fig. 3b shows the effect of some low-temperature hydration cycles on the repetitive reactions. After a stable reactivity was attained at a high hydration temperature of 150 °C after 15 cycles of repetition, the cycle was subjected to low-temperature hydration at 130, 110 and 90 °C, and the high-temperature hydration was resumed at the 19th cycle. The extent of hydration after reversion to these conditions was not affected by the low-temperature hydration experience; and reactivity at the 19th cycle reverted to a similar value to that at the initial cycle. The effect of multiple hydration conditions on the repetitive durability is shown in Fig. 4. The standard repetition at 110 °C and 47.4 kPa was followed by multiple hydration conditions at 110–170 °C and 31.2–70.1 kPa from the 8th to the 19th cycle. Following this, it was found that the reactivity under standard conditions at the 20th cycle was maintained or enhanced compared with the value at the initial cycle.

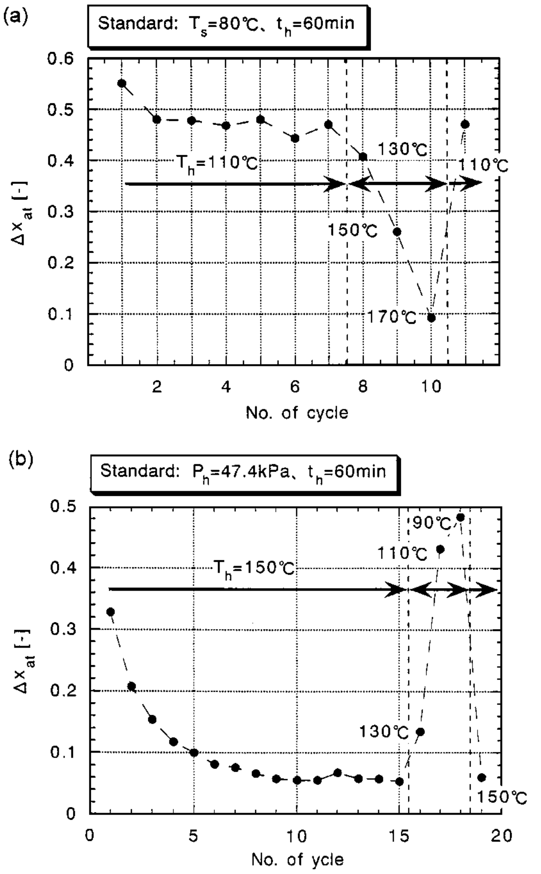

Figure 3 Effect of change in hydration conditions on the repetitive durability; (a) the effect of high hydration temperature cycles on the low temperature cycle, (b) the effect of low hydration temperature cycles on the high-temperature cycle.

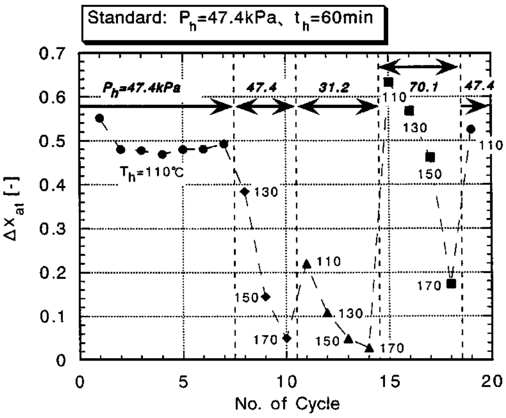

Figure 4 The effect of multiple hydration temperature cycles on a standard cycle.

4. Discussion

4.1. Evaluation of reactivity change during the repetition

Between shrinking-core models under a pseudo-steady-state [5], a model of diffusion through product controlling was the most suitable to the hydration reaction system in a previous study [4]. The rate equation based on the model is,

$$\frac{1}{t^*}t = 1 - 3(1 - x_\mathrm{h})^{2/3} + 2(1 - x_\mathrm{h}) \tag{6}$$

where t^* represents a characteristic time [s].

$$t^* = \frac{\rho r^2}{6C_\mathrm{V}D_\mathrm{V}} \tag{7}$$

ρ [kg/m^3], r [m], C_V [kg/m^3], D_V [m^2/s] are the density of solid reactant, radius of the particle, the bulk concentration of vapor and the effective diffusivity of vapor. This model was employed for the reaction mechanism and is used in the following discussion.

The value of the reciprocal of the characteristic time, $1/t^*$, is obtained as the slope of the linear plot of the right hand side of Equation 6 against t in each experiment, and corresponds to the reactivity of the hydration. To evaluate reactivity change during repetitive cycle, a value of $1/t^*$ is used as an index of the hydration reactivity. Fig. 5 shows the relationship between the hydration temperature and $1/t^*$ of the first cycle and the tenth cycle. The values of the tenth cycle are used as representatives of the saturated steady state values for the repetition, for comparison with the initial reactivity. The higher the temperature, the lower is the value; that is, the reactivity. Next, a ratio index (η[-]) is introduced

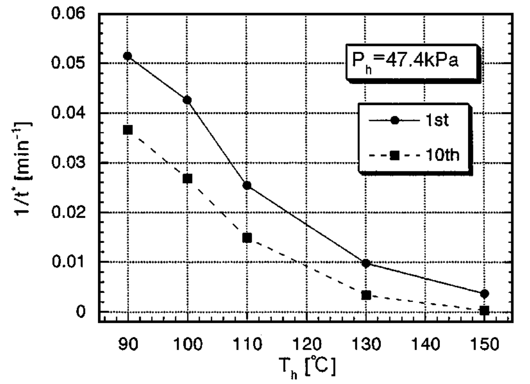

Figure 5 Change of effect of the hydration temperature on $1/t^*$ from the first cycle to the tenth cycle.

to describe the effect of cycle repetition on the reactivity as follows:

$$\eta = [1/t^*]_{10\text{th}}/[1/t^*]_{1\text{st}} \tag{8}$$

where the tenth cycle's value is used to characterize the saturated stable state of the repetition. The index shows the durability of the sample's reactivity in repetitive cycling. The effect of hydration temperature on the index is shown in Fig. 6a. The lower the hydration temperature, the larger the index and, the better the durability. Fig. 6b shows the relationship between the reaction pressure and the ratio index. The index increases with pressure; a higher reaction pressure leads to greater repetitive reactivity.

4.2. Microscopic observation

To explain the relationship between the repetitive cycle condition and the hydration reactivity, two reaction samples, which had experienced low and high durability cycle conditions, were compared by microscopic observation. Each bulk particle used in the experiment is a cluster of primary particles having diameter of 300–700 nm. Since the two samples exhibited no obvious differences in these bulk and primary particles, the interior of the primary particles were examined. Fig. 7 shows TEM photographs of sectional particles. Fig. 7a shows a sample cycled at 57.9 kPa hydration pressure, representing results of high durability cycle conditions. Fig. 7b shows a sample cycled at 31.2 kPa, representing one of low durability conditions. Both samples were in the hydroxide state after twelve cycles at a hydration temperature of 110 °C. In Fig. 7a, nuclei of a few nm diameter can be observed over the whole area. Although similar nuclei are seen in a part of the later sample in Fig. 7b, they are not developed over the whole area. MgO and $Mg(OH)_2$ have a square and hexagonal crystal structure respectively [6]. The nuclei are produced by the structure change between MgO and $Mg(OH)_2$ during the repetitive cycling. Such nuclei had been observed in a previous study [7]. Because the nucleation is accompanied by the generation of a high reaction surface area, the development of sufficient nuclei shows that the former cycle reaction has proceeded enough and also the next cycle has high reactivity.

Because of high reactivity at the low hydration temperature in Fig. 7a, the nucleation proceeded well at

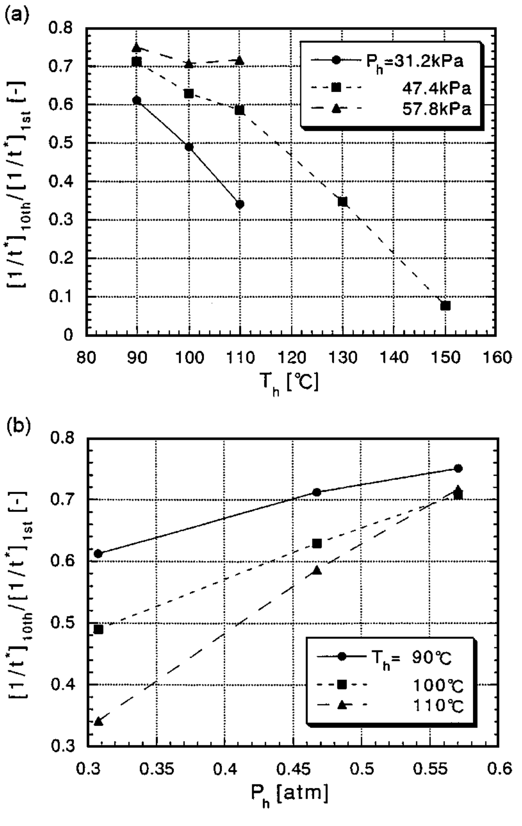

Figure 6 Change of the ratio index, η; (a) dependency on the hydration temperature, (b) dependency on the hydration pressure.

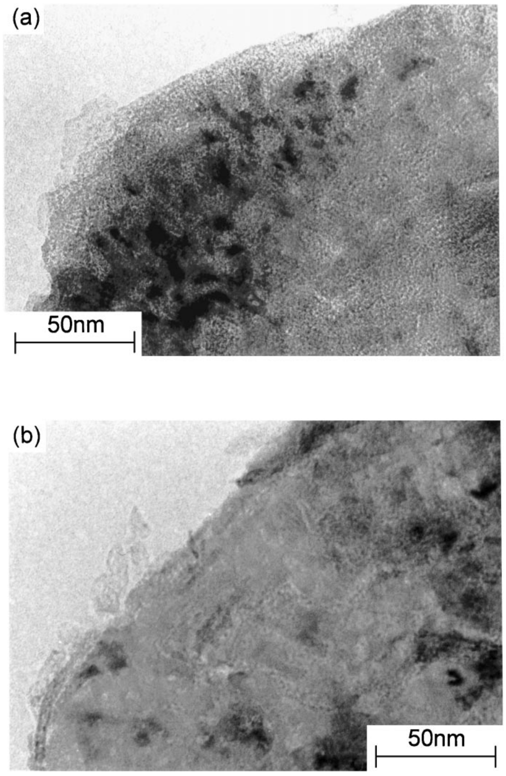

Figure 7 TEM photographs of hydroxide state samples after twelve repetitive cycles at the hydration temperature of 110 °C; (a) a sample particle at 57.9 kPa of hydration pressure representing a high durability cycle condition, (b) a sample at 31.2 kPa representing low durability cycle condition.

the hydration step, and generated fully-developed nuclei in the primary particle. The particle acquired a high reaction surface area and diffusivity, and so the reactivity was sustained during the repetitive reaction. On the other hand, the low reactivity at the high hydration temperature in Fig. 7b did not induce the structure change and the nucleation. Moreover, sintering inside the particle [7] proceeded during repetitive cycles. At the next cycle of hydration, similar reactivity could not be maintained because of the small amount of reaction surface area and diffusivity accompanying the nucleation. Then, the repetitive durability was lost gradually. However, the sintering state could be fractured under high-reactivity condition cycle, as shown in Figs 3a and 4.

The reaction condition dependency of the hydration repetitive reactivity is explained by the nucleation mechanism. That is, a higher reactivity condition leads to greater repetitive durability, because the higher reactivity leads to greater nucleation during repetition and the nucleation leads to greater reaction surface area and higher diffusivity for the reaction. Because a lower temperature leads to greater reactivity, the lower the temperature, the better the durability is in Fig. 6a. Durability increases with pressure, as seen in Fig. 6b. On the other hand, when nucleation proceeds sufficiently during the repetitive reaction, the repetition would maintain the reaction durability. Therefore, the identification of the nucleation is an important criterion in deciding the appropriate repetitive cycle conditions for the heat pump operation.

5. Conclusion

The developed reaction material showed durability during repetitive magnesium oxide/water reversible reaction at 90–110 °C hydration temperature and under 47.4–57.8 kPa hydration pressure. The saturated durability was reproducible under the same hydration temperature and pressure conditions in the repetitive cycle, and was not affected by the experience of different reaction conditions in the cycle. The repetitive durability was explained from the standpoint of the nucleation in a primary particle of the material. Sufficient development of nucleation was an important factor in the enhancement of the repetitive durability.

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