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Thermal conductivity-controlled Zn-doped MgO/Mg(OH)₂ micro-structures for high-efficiency thermo-dynamic heat energy storage

SOCIETY OF JAPAN

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ABSTRACT

Zn-doped MgO/Mg(OH)₂ was used to increase thermal energy storage efficiency. Among general bulk materials, the thermal conductivity of those materials used for high-efficiency thermal energy storage should be high. In micro (or nano) structures, however, the lower the thermal conductivity, the heat can be more easily concentrated on the surface, enabling a thermodynamic reaction to store heat energy to be easily induced. Zn-doped MgO limits the vibration of the lattice and ultimately lowers the thermal conductivity. This reduced thermal conductivity increases the surface heat accumulation, and it was confirmed that dehydrogenation of Mg(OH)₂ surfaces can occur rapidly, increasing the thermal energy storage efficiency.

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Thermal energy storage; Zn-doped MgO (Mg_{1-x}Zn_xO); thermal conductivity

1. Introduction

As high-level industrialization proceeds, conventional power plant systems are causing serious environmental pollution problems, such as extreme emissions of CO₂ gas from fossil fuel consumption and issues involving disposal of nuclear waste [1-4]. Many studies of alternative energy sources, that can be converted from natural environmental sources such as solar, wind, and hydroelectric power, have been carried out [5-13]. However, these power sources are unpredictable (and prone to severe fluctuation depending on the time and area), resulting in growing demand for real-time energy storage systems. A commonly used method of storing various types of energy is to first convert it into kinetic energy and, finally, to store it in the form of electrical energy in batteries [14,15]. However, if we convert thermal energy into electrical energy, the conversion loss from the energy conversion process can be extremely large. Therefore, there is a need for a method of storing thermal energy in its original form without converting it into electrical energy.

There are several types of thermal energy storage reactions (based on endothermic and exothermic reactions), such as metal hydration, transition metal carbonation or oxidation, ammonia-based chemical reaction, and alkaline earth metal oxide hydration [16]. Of these, the alkaline earth metal oxide hydration reaction is most economical. The reactants are stable, and the temperature required for the thermochemical reaction, especially in MgO/Mg(OH)₂ systems, is only 300 °C; it is therefore expected to be applicable in various fields. The most serious problem in applying MgO/Mg(OH)₂ systems in actual industrial or application fields is that the heat

transfer efficiency of the reaction is not very high due to the low thermal conductivity of MgO and Mg(OH)₂ [17-25]. Because low thermal conductivity can reduce efficiency by disturbing the heat flow to the inside of the materials employed in MgO/Mg(OH)₂ systems. However, if we can effectively synthesize small particles from the nano to the micro size on surface of specific structures, this issue can be inversely resolved. When the nano- or micro-sized Mg(OH)₂ can be attached to a micro-beam, it is necessary to lower the thermal conductivity to enable the heat flow into the interior of micro-beam to be minimized, and the reaction on the surface to be maximized by heat accumulation. In general, the thermal conductivity of insulator ceramics is caused by a lattice vibration. Therefore, when the lattice vibration is reduced by doping MgO with ions that have a different ionic size from Mg^{2+} , the thermal conductivity can be lowered. In this study, we experimented with doping Zn, which is known to be easily doped to MgO (Mg_{1-x}Zn_xO, x = 0, 0.1, 0.2, and 0.3), and then fabricated micro-sized structures using the electron beam irradiation method [26]. It was confirmed for the first time that heat-storage efficiency can be increased in a micro-sized MgO/Mg(OH)₂ system with reduced thermal conductivity.

2. Experiment

2.1. Fabrication of $Mg_{1-x}Zn_xO$ micro-sized beams with $Mg(OH)_2$ flakes

ZnO and MgO oxide powders were used as starting materials, with various concentrations of ZnO in MgO ranging from 0 to 30 at% (0, 10, 20, and 30 at%). These powders were mixed with ethanol by ball-milling for

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6 hours. After drying, the powders were pressed into disks with a diameter of 10 mm and thickness of 1 mm. The disks were sintered at 1000°C for 4 hours in air. A carbon crucible (volume of 7 cc and thickness of 2 mm (KOREA VACCUM TECH, KOREA)) filled with Mg_{1-x} Zn_xO pellets was loaded in a vacuum chamber of $\sim 10^{-6}$ torr. To achieve uniform irradiation, electron beams with an emission current of 40 mA were applied to the various positions in a carbon crucible divided into nine areas. The irradiation time applied to each area was $1 \sim 2$ mins. Mg(OH)₂ was synthesized on the micro-beam by immersing e-beam irradiation Mg_{1-x}Zn_xO pellets into a solution of 0.4M MgCl₂ H₂O at 80°C for 2 hours. For detailed method used for fabrication of the micro-beam and synthesis of Mg(OH)₂, refer to our previous report [26].

2.2. Analysis

Mg_{1-x}Zn_xO pellets were measured by X-ray diffraction (XRD; HD30772, Rigaku, Japan) analysis to confirm whether the ZnO and MgO were segregated. The relative Zn atom content and surface morphology of each molar ratio were analyzed by scanning electron microscope and energy dispersive X-ray spectroscopy (SEM; JSM-500HR, JEOL, Japan). To analyze with laser flash apparatus (LFA; LFA457, NETZSCH, USA), the pellets were ground in $5 \times 5 \times 1$ mm rectangular shapes. After of one side of the ground pellets, the thermal diffusivity was measured from the heat signal on the opposite site in real time. The specific heat capacity was measured by differential scanning calorimetry (DSC, DSC 200 F3 Maia, NETZSCH, USA).

The density was calculated by measuring the weight and volume of the samples separately. All the measurements of conductivity except the density measurement were carried out in real time for each temperature. Density is also a function of temperature, but measurements based in temperature exclude thermal expansion. Finally, the thermal conductivity was estimated by equation (1) (σ : thermal conductivity, ρ : density, D: thermal diffusivity, c_p : specific heat capacity). Thermal analysis was performed in N₂ atmosphere using thermal gravimetric analysis and differential thermal analysis (TGA, DTA; DTG-60H+FC-60A+TA-60W, SHIMADZU, Japan).

$$\sigma(T) = \rho \times D(T) \times c_{\rho}(T)$$
(1)

3. Result

First, when $Mg_{1-x}Zn_xO$ was synthesized through Zn doping, the crystallinity was confirmed by XRD. (See the XRD pattern shown in Figure 1(a)). When the doping concentration was increased from 0% to 30%, only the peaks of rock salt-structured MgO could be identified, and neither ZnO with a hexagonal-based Wurtzite structure nor other secondary phases were observed at all. Therefore, it seemed to be completely mixed with

substitution of Zn^{2+} ions to the Mg^{2+} site. A comparison of the pellets of pure MgO (x = 0) and $Mg_xZn_{1-x}O$ showed that the (111) peak intensity of the pellets containing Zn was higher than that of those containing pure MgO. The diffraction intensity (F) of the rock salt structure was determined by equation (2) when the index of the crystal plane was odd, and by equation (3) when it was even [27]. As the atomic structure factor (f) of Zn is larger than that of Mg, the ratio of (111)/(200) could be increased because the intensity of (111) increases when Zn is substituted with Mg. In the inset of Figure 2(a), the (111) peak is shifted to a lower angle with doping. this means that Zn increased the plane spacing:

$$F_{odd} = 4 \big[\big\{ (1-x) \cdot f_{Mg} \,_+ x \cdot f_{Zn} \big\} - f_O \big] \tag{2}$$

$$F_{even} = 4 \big[\big\{ (1-x) \cdot f_{Mg} \,_+ x \cdot f_{Zn} \big\} + f_O \big] \tag{3}$$

In the quantitative analysis of the element by EDS (Figure 1(b)), it was also confirmed that the Zn La peak increased with the increases in the doping concentration. The reason why the amounts of doping differed from the amounts of element in EDS quantitative analysis was judged to be due to various variables (such as surface roughness) that can occur in EDS measurement.

The thermal conductivity of a solid material is calculated as the product of its specific heat capacity, density, and thermal diffusivity. When Mg²⁺ (72 pm) of the MgO octahedral site was replaced with Zn²⁺ (75 pm) [28,29], it induced stress in the lattice to restrict lattice vibration, i.e., phonon migration. Thus, the data in Figure 2(a,b) show that the specific heat capacity and thermal diffusivity decreased with increases in the Zn doping concentration. Also, the general physical phenomena in which the thermal capacity and thermal diffusivity decrease due to increases in phonon scattering with increases in temperature were also accurately measured. In addition, the densities measured according to the Zn doping concentration were 3.253 (10% doped), 3.499 (20% doped), and 3.980 g/cm³ (30% doped), respectively. As the doping concentration rose, the density was increased by the relatively heavy Zn atoms. The calculated thermal conductivity (Figure 2(c)) decreased with increases in the Zn doping concentration and decreased from 8.136 W/m K (10% doped) to 4.786 W/m K (30% doped) at room temperature.

The $Mg_{1-x}Zn_xO$ was subjected to e-beam irradiation for surface microstructure formation. (See the schematic in Figure 3(a)). After high-energy electron surface irradiation, the surface roughness of $Mg_{1-x}Zn_xO$ increased due to random sublimation. When the irradiation position was changed, the equilibrium vapor pressure difference according to the local temperature gradient caused re-solidification on the rough surface, resulting



Figure 1. (a) XRD patterns (figure of inset comparing the (111) plane peak), (b) EDS spectra, and (c) table of the $Mg_{1-x}Zn_x$ O concentration according to the ZnO concentration.

in micro-structure formation on the $Mg_{1-x}Zn_xO$ surfaces, as shown in Figure 3(b). The shape of micro-structure was cuboid beam, because the (111) plane of the rock-salt crystal structure is energetically unstable due to the polarity, and a stable (100) plane is ultimately formed on the surface [30–32]. The shape and thickness of the micro-beam according to the doping concentration clearly did not vary greatly, because the same crystal structure was maintained after doping.

After synthesizing the brucite $Mg(OH)_2$ nano-plates on the micro-structural $Mg_{1-x}Zn_xO$ surface (see the Experimental section and the inset in Figure 4(a)), thermal analysis was conducted. The DTA data in Figure 4(a) show that as the Zn doping concentration increased, the endotherm peaks shifted to lower temperatures. It can be seen that a dehydration reaction occurred relatively quickly due to the rapid accumulation of heat on the surface of the micro-beam after doping with Zn, which has lower thermal conductivity. For this reason, it can be confirmed that the mass reduction, which can be confirmed by TGA data

(Figure 4(b)), increased with increase in the Zn doping concentration. In this experiment, the changes in the mass of Mg(OH)₂ in the pyrolysis process can be attributed to decomposition of water molecules occurring when desorption of the atmospheric gas adsorbed on the solid surface was negligible. The mass change of 30% Zn-doped MgO shown in Figure 4(b) is about 4.073 mg, which translates to 2.26 \times 10⁻⁴ moles of water molecules. Therefore, it can be seen that the mole number of Mg(OH)₂ required for desorption of 4.073 mg of water molecules is the same as the 2.26×10^{-4} observed in consideration of the reaction coefficient $(Mg(OH)_2 (s) \rightarrow MgO (s) + H_2O (g))$ Δ H= 81kJ/mol) [16]. Since Mg(OH)₂ can store 81 kJ of energy per mole, it can be deduced that 18.3 J of energy was stored in our experimental results. Considering that the average weight of the Mg_{1-x}Zn_x O pellets used in this experiment was 137.23 mg, the thermochemical storage energy per unit mass was calculated to be about 133.23 kJ/kg, which is higher than the value reported in our previous report [26].



Figure 2. (a) DSC data, (b) LFA data of the $Mg_{1-x}Zn_xO$ according to the ZnO concentration, and (c) thermal conductivity calculated by DSC, LFA, and density.

$$hA(T_{\infty} - T) + kA\frac{dT}{dx} = \rho cV\frac{dT}{dt}$$
(4)

In order to consider the possibilities of the concept in more varied ways, we conducted a numerical of calculations method using a differential equation. The calculations assumed the case of heating through convection to a micro-beam with a width of 10μ m. The differential equation used for the calculations is shown as Equation (4) (The parameters of equation (4) are as follows; h: convection coefficient, k: thermal conductivity, ρ : density, c: specific heat capacity, A: area, V: volume). The calculation results in Figure 5 show the temperature distribution from the center to the surface of the microbeam. And each parameter in the calculations was our measured value. The results of the calculations that as the thermal conductivity became lower with doping, the temperature gradient between the interior and surface of the micro-beam grew larger. This indicates that the heat can be accumulated on surface.



Figure 3. (a) Schematic illustration of the e-beam irradiation process and (b) SEM images of $Mg_{1-x}Zn_xO$ surfaces after e-beam irradiation.



Figure 4. (a) TGA and (b) DTA data for $Mg_{1-x}Zn_xO$ according the ZnO concentration; the SEM image in inset (a) is of an $Mg(OH)_2$ plate on a micro-beam.



Figure 5. Calculated distribution of temperatures of microbeam from center to surface.

4. Conclusions

This study presents a method of increasing the efficiency of MgO/Mg(OH)₂ thermal energy storage systems using doping. Zn ions can be uniformly doped up to a 30% concentration in the MgO lattice without forming second phases. Zn-doped MgO limits vibration of the lattice and ultimately lowers the thermal conductivity. Reduced thermal conductivity increases the surface heat accumulation, and it was confirmed that dehydrogenation can occur rapidly on Mg_{1-x}Zn_x O micro-beam surfaces, increasing the thermal energy storage efficiency. Unlike conventional bulk scale thermal energy storage systems. this method of lowering the thermal conductivity of materials can be applied to improve the efficiency of nano- or micro-sized heat energy storage systems.

Disclosure statement

The authors declare no competing financial interests.

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