

## Article

# Novel Sodium Chloride/Aluminum Oxide Powder-Composite Structure with High Shape-Retention Performance for the Encapsulation of a High-Temperature Phase-Change Material

Seiji Yamashita <sup>1,\*</sup>, Bao Fuhai <sup>2</sup>, Liao Shenghao <sup>2</sup>, Hideki Kita <sup>2</sup> and Fangjun Hong <sup>3</sup>

<sup>1</sup> Department of Materials Process Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

<sup>2</sup> Department of Chemical Systems Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan; baofuhai1993@yahoo.co.jp (B.F.); liao\_shenghao@yahoo.co.jp (L.S.); kita.hideki@material.nagoya-u.ac.jp (H.K.)

<sup>3</sup> School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China; mehongfj@sjtu.edu.cn

\* Correspondence: yamashita.seiji@material.nagoya-u.ac.jp

**Abstract:** Inorganic phase-change materials (PCMs) with high melting points have great potential for thermal energy storage systems. Sodium chloride (NaCl) has a high melting point (801 °C) and high latent-heat-storage density (482 kJ/kg). However, it is difficult to encapsulate NaCl using a sintered ceramic shell because of its good wettability against ceramics and high volume-expansion capacity during melting. In this study, a novel NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite structure was developed as highly stable PCM core material for highly stable encapsulation. The shape-retention performance and the mechanism of NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite structure during melting were investigated. We have successfully fabricated a NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite structure, which has a higher NaCl volume ratio of 80 vol% than conventional techniques. The gel-like network structure of Al<sub>2</sub>O<sub>3</sub> particles in molten NaCl was a key structure to keep the shape of the composite ball and to prevent the evaporation of molten NaCl.

**Keywords:** inorganic PCM; powder composite; shape retention; NaCl; Al<sub>2</sub>O<sub>3</sub>



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## 1. Introduction

Thermal energy storage (TES) has many potential applications including solar thermal-power generation, industry-waste-heat recovery, thermal comfort in buildings, and the packaging of thermally sensitive materials, and hence it has attracted considerable attention over the past few decades [1]. Inorganic phase-change materials (PCMs) have great potential for thermal energy storage (TES) because of their low cost and high heat-storage density. In particular, high-melting-point phase-change materials, such as chloride salts [2–4], fluoride salts [2,3], and carbonate salts [2,3] for high-temperature heat-storage systems are required. To utilize inorganic PCMs for TES, the PCM-composite structure must include carriers such as ceramics [5–7], graphite [8], or metal [9]. However, it is difficult to maintain shape and chemical stability during melting and solidification at high temperatures. Sodium chloride (NaCl) has great potential as a latent-heat-storage material for high temperatures; it has a high heat-storage density of 482 kJ/kg and a high melting point of 801 °C [2]. There were some researchers reported that the contact angle of molten NaCl or other chloride to a sapphire (100) substrate was 0 deg [10–12]. In a core-shell structure using a NaCl core and Al<sub>2</sub>O<sub>3</sub> shell, it seems to be impossible to prevent the leak of molten NaCl because of the excellent wettability of molten NaCl against the Al<sub>2</sub>O<sub>3</sub> surface. Furthermore, another reason why it was difficult to make an encapsulation structure is that the volume expansion during the phase change from solid to liquid for NaCl was quite large at around 39.4% [10]. There is some research regarding the composite structure of

porous ceramic material and inorganic PCMs. Yue Qin et al. have also reported sodium sulfate diatomite-composite materials which have a thermal-storage density of 146 kJ/kg at 900 °C [5]. Yong Li et al. have reported nitrate composite/SiC ceramic honeycomb which has a thermal-storage density of 103 kJ/kg at 220 °C [6]. These PCM composites were made by impregnating molten PCM into a porous ceramic body with a porosity of about 50 to 70%. However, these PCM/porous ceramic-composite materials were needed to control the pore-size distribution and porosity of ceramic carriers, and there are problems such as a low concentration of PCM and the manufacturing costs of these carriers. Although inorganic salt PCMs and ceramics or graphite powder composites in the medium temperature range have been reported, the volume fraction of carriers was still high at around a 40 vol%, as is the case of ceramics porous carriers [13]. A few research endeavors have reported the entire technique for high-temperature inorganic PCMs using ceramic [14] or graphite [8] shell materials. This research also needs to cover the complex processes of creating the capsule and encapsulating PCMs. These carrier materials such as porous ceramics or ceramic capsules were only used to keep the shape of molten PCMs. From the view point of heat-storage performance, these carrier materials should be minimized. Therefore, a novel PCM-composite structure that can stably combine PCMs at high concentrations and high temperatures is required. On the other hand, the composite of metal oxide nanoparticle such as CuO, ZnO and Al<sub>2</sub>O<sub>3</sub> and inorganic PCM was also reported to improve the thermal conductivity and thermal diffusivity [15,16]. The improvement of heat transfer and heat capacity of the composite of PCMs with ceramic particles was evaluated experimentally and using a molecular dynamics simulation which reported increases of 40.82% and 44.23%, respectively [17]. Therefore, a composite of PCMs with ceramic particles could be very useful for heat-storage-material applications. In these studies, concentrations of nanoparticles that improve thermal properties are reported to be less than 10 vol%, and there are a few reports on systems with submicron- to micron-sized particles in PCM composites. Furthermore, there are few reports on the shape retention of samples during their PCM melting.

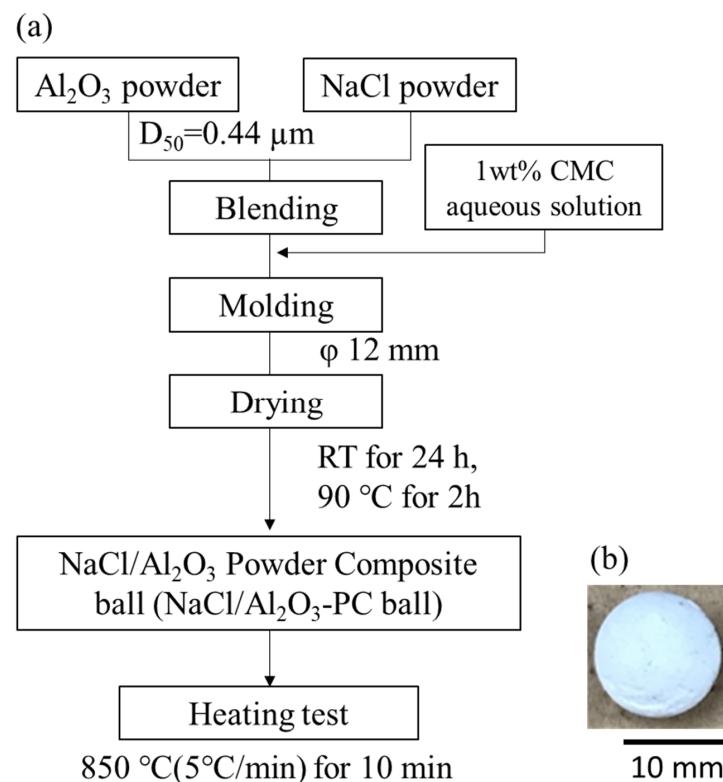
Regarding the fabrication methods of the composites of inorganic PCMs and ceramic particles, a cold sintering process (CSP) [18,19] and chemical reaction method [20] have been reported. The CSP could fabricate the composite of inorganic PCM and metal oxide particle with high relative density ~98% for low temperatures compared with conventional sintering methods. The NaCl/Al<sub>2</sub>O<sub>3</sub> composite for the application of PCM which was fabricated using the CSP was also reported. Bilyaminu S. et al. [21] reported that NaCl-Al<sub>2</sub>O<sub>3</sub> (50–50 wt%)-composite material has a high relative density of 98.65% and latent-heat-storage density of 252 J/g, which have been fabricated using CSP. Fracture strength tests showed a high sintering strength of approximately 5 GPa after 50 min. The composite material showed low mass loss due to volatilization during a heating–cooling-cycle test. However, the CSP method requires press molding at a high pressure of about 400 MPa, which is considered a challenge in terms of the mass production and flexibility of the shape. Heat-storage bodies are required to have various shapes depending on their applications. For example, spherical heat-storage materials are preferred for TES based on a packing bed such as a regenerative burner system [22,23] or solar-concentrated solar-power (CSP) plants [24,25]. Therefore, a simpler method to fabricate heat-storage spheres is needed. Furthermore, there have been reports on the thermal properties of these composite materials, but no reports on their shape retention over the melting temperature of PCM. If the shape retention of inorganic salt-based PCMs during melting can be improved, the range of materials for shell-material selection or shell-fabrication methods will be expanded when making an encapsulated thermal-storage ball. Especially for PCM for heat storage in the high temperature range of 600 °C or higher, ceramic materials are the only choice for the shell material. Since the sintering temperature of many ceramic materials is higher than the melting point of PCMs, most of them are sealed by filling the PCMs with a shell made of sintered ceramics, which makes the shell thicker, resulting in a lower heat-storage density. Therefore, if PCMs with high shape retention and low leakage can be fabricated in the

molten state such as in the present study, high-temperature processes such as simultaneous sintering of core-shell bodies, which have been difficult in the past, can be used.

In this research, an NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite structure was developed as a novel PCM/ceramic-composite PCM with high shape retention over the melting temperature of NaCl. By developing this PCM, which has high shape retention even in the molten state, it can be used as an encapsulated PCM heat-storage core even with a simple shell that is not a sintered body as in the conventional researches. The leakage of molten NaCl with different concentrations of ceramic particles is evaluated, and we determine the optimal particle concentration to minimize leakage. The effects of particle size and wettability against molten NaCl of ceramics powder on the shape-retention performance and leakage of molten NaCl are also evaluated. Furthermore, the mechanism of the shape retention of the composite structure of molten NaCl and Al<sub>2</sub>O<sub>3</sub> particles are discussed.

## 2. Experiment

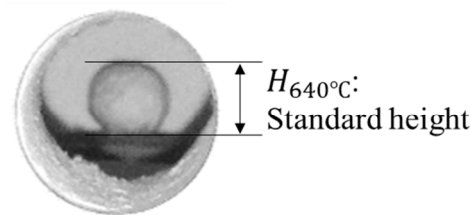
Al<sub>2</sub>O<sub>3</sub> powder (AES-12, Sumitomo Chemical Co., Tokyo, Japan) and NaCl powder was mixed at predetermined volume concentrations of 60, 70, 80, and 90 vol%NaCl. The NaCl/Al<sub>2</sub>O<sub>3</sub> powder composite was molded into a resin mold with a diameter of 12 mm together with 1 wt% CMC (Granulation Binder, CMF-7, ASONE, Nagoya, Japan) aqueous solution. After drying at room temperature and 90 °C for 1 h, it was demolded to obtain a NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite (PC) ball as shown in Figure 1. The packing rate of NaCl/Al<sub>2</sub>O<sub>3</sub> is adjusted in the range of 0.65 to 0.80. In order to check the stable encapsulation using a simple non-sintering ceramic shell, SiC castable cement (DrySiC-85D-RE, AGC Inc., Tokyo, Japan) was used for the coating shell material of the NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball. The NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball was coated with SiC castable cement slurry, which was mixed with the distilled water of the same weight, and dried at 90 °C for 1 day. To evaluate the effect of particle size and the wettability of the material against molten NaCl with leakage of NaCl and shape-retention performance, Al<sub>2</sub>O<sub>3</sub> (D<sub>50</sub> = 11.9, 58.6 µm; WA#240, WA#1000, FUJIMI Incorporated, Kiyosu, Japan) and h-BN (D<sub>50</sub> = 0.7, 11 µm; UHP-S1, UHP-1K, RESONAC, Tokyo, Japan) were used as ceramic powders.



**Figure 1.** (a) Experimental procedure and (b) appearance of NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite ball.

The obtained NaCl(80 vol%)/Al<sub>2</sub>O<sub>3</sub>(20 vol%) PC ball and NaCl ball were heated at 5 °C/min until 850 °C for 10 min on the SiC castable substrate in a furnace. The shape of the NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball and NaCl ball during heating was photographed to evaluate the shape change over the melting point of NaCl. The sample was placed at the back side of a small electric furnace (Inside: 70 mm × 120 mm × 50 mm) with a peephole (Diameter: 20 mm), and the appearance of the sample during heating was photographed using a camera from the outside through the peephole. The temperature in the furnace was measured using a thermocouple which was placed in the furnace. The shape-change rate  $\Delta H$  was defined as the height of the NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball at each temperature;  $H_t$  was measured using image analysis normalized with the height at 640 °C.  $H_{640^\circ\text{C}}$  was as shown in Figure 2.

$$\Delta H = \frac{H_t}{H_{640^\circ\text{C}}} \quad (1)$$



**Figure 2.** The definition of shape retention  $\Delta H$ .

The weight change of the NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball was also measured before and after heating at 850 °C. To evaluate the stability during heating over the melting point of NaCl, the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC ball was heated at 850 °C for 10 h, and we measured the weight change before/after heating. The microstructure and composition in the cross sectional face of the NaCl/Al<sub>2</sub>O<sub>3</sub> PC ball before and after heating was observed using FE-SEM/EDS (JSM-7500F, JEOL, Tokyo, Japan) and XRD (Ultima IV, Rigaku, Tokyo, Japan). The cross sectional face is made using mechanical cutting and polishing with abrasive cloth #1200 without water solvent. The heat-storage performance of the samples was recorded using TG-DTA(DTG-60AH, SHIMADZU, Kyoto, Japan). Heating conditions are raised to an 850 °C atmosphere at a rate of 10 °C/min and held for several minutes. The NaCl powder and NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-composite samples were prepared in an alumina cell container and measured. Al<sub>2</sub>O<sub>3</sub> powder, adjusted to have equal heat capacity, was used as the standard sample.

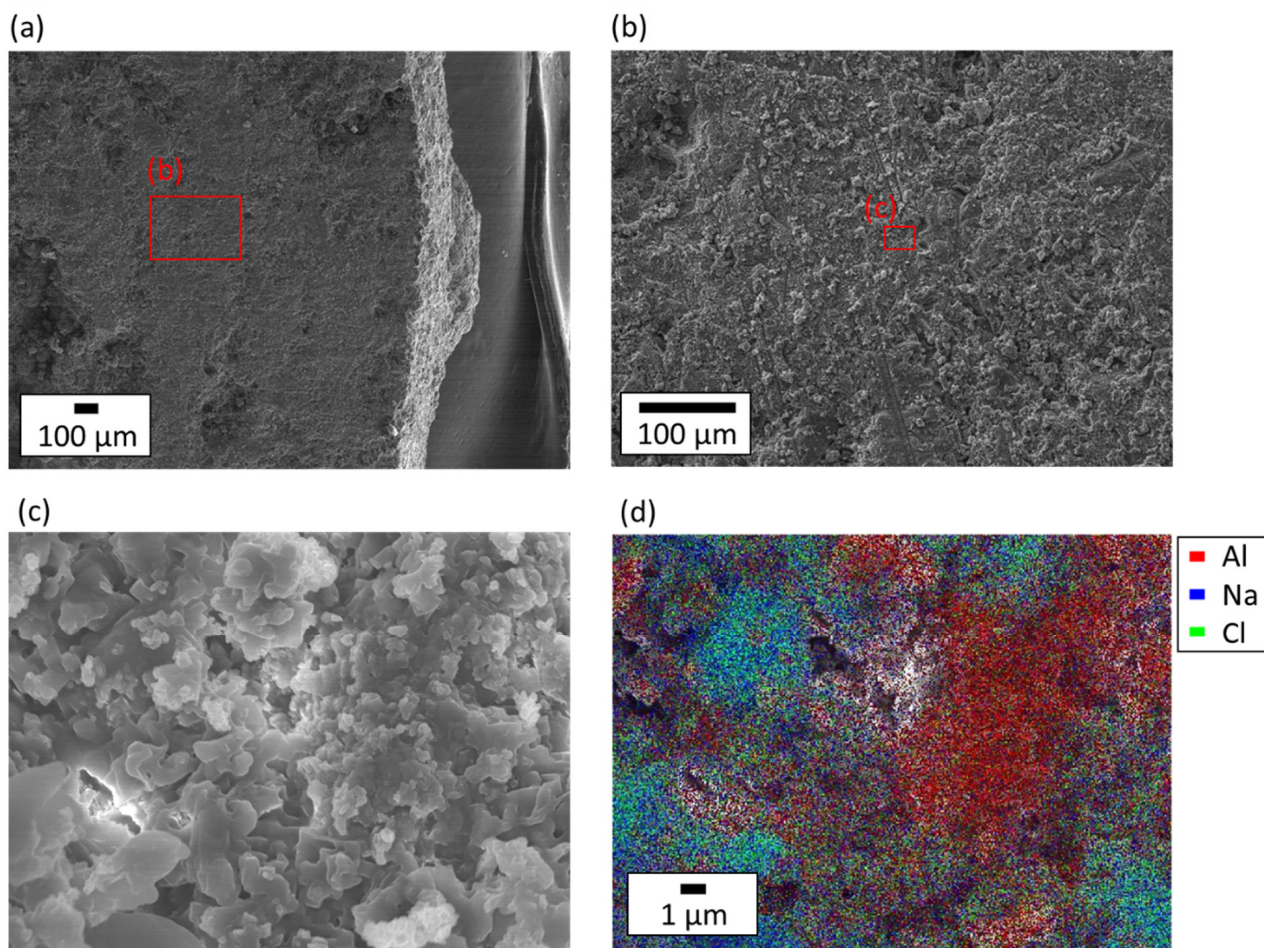
### 3. Results and Discussion

#### 3.1. Shape-Retention Performance and Heat-Storage Property of NaCl/Al<sub>2</sub>O<sub>3</sub>-PC Structure

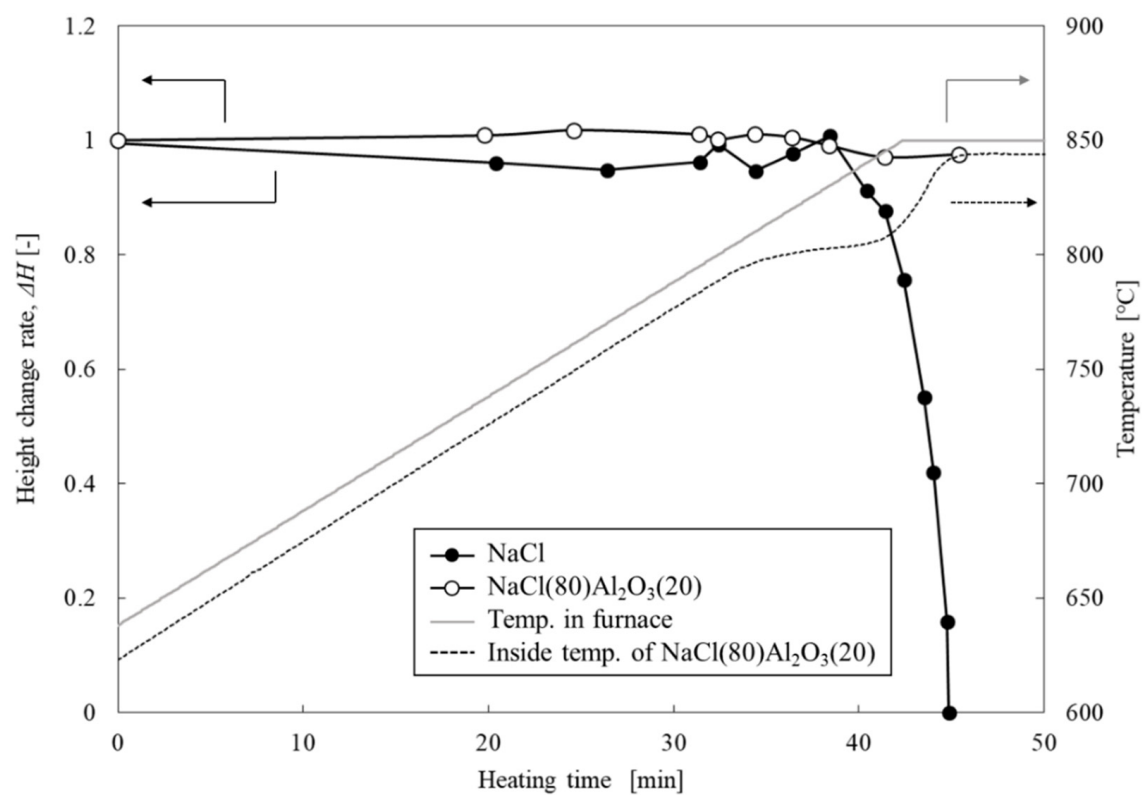
Figure 3 show SEM/EDS images of the cutting surface of the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball before heating. From element analysis images in Figure 3d, NaCl and Al<sub>2</sub>O<sub>3</sub> particles were composited uniformly, and there are no large pores because of the high packing rate of 0.82. The strength of the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball was hardly recorded. In Figure 4, the height-change rates of the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball and NaCl ball during heating in the furnace are shown. In the case of the NaCl ball, the height-change rate  $\Delta H$  was sharply decreased by melting when the temperature reached 801 °C. Molten NaCl was evenly spread on the SiC castable substrate as shown in Table 1. In the case of the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball, it is found that  $\Delta H$  did not change almost at all even though NaCl was surely melted due to the temperature. In Table 1, the shape of the NaCl/Al<sub>2</sub>O<sub>3</sub>-PC ball was almost not changed until the temperature reached 850 °C. The viscosity of the molten NaCl was 1.2 mPas at 801 °C [12], which is too low to be kept in shape, as is shown in the heating test of the NaCl ball in Table 1. In the cutting face of the NaCl/Al<sub>2</sub>O<sub>3</sub>-PC ball after heating, as shown in Figure 5, there was a network structure of Al<sub>2</sub>O<sub>3</sub> micro particles in a NaCl matrix and many large pores. This means that Al<sub>2</sub>O<sub>3</sub> particles in liquid NaCl caused a gel-like network aggregation without dispersion. It is



assumed that the  $\text{Al}_2\text{O}_3$  particles did not dissolve or react with molten NaCl because the diameter of  $\text{Al}_2\text{O}_3$  particles did not change compared with the primary particle size of  $0.44\ \mu\text{m}$ . The TG-DTA results of NaCl and NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC are shown in Figure 6. Two peaks were identified in the DTA curve of NaCl. The sharp peak around  $801\ ^\circ\text{C}$  is the melting point of NaCl, and the broad peak starting around  $900\ ^\circ\text{C}$  is considered to be the latent heat of evaporation of molten NaCl. On the other hand, the NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC sample showed only an endothermic peak starting around  $801\ ^\circ\text{C}$  due to NaCl melting, indicating that the evaporation of NaCl is suppressed by the  $\text{Al}_2\text{O}_3$  particle composite. The TG curve trend also showed a significant difference between these two samples, with NaCl showing a rapid weight loss above the melting point, whereas the weight loss of NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC was slower. These results are consistent with the shape-retention results shown in Figure 4, and confirm that the NaCl/ $\text{Al}_2\text{O}_3$  powder-composite structure is more stable than the NaCl material alone, even when melted. The latent heat of each sample calculated from the peak areas were NaCl:  $461\ \text{J/g}$  and NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC:  $267\ \text{J/g}$ . This is calculated from the NaCl concentration in the NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC: 68 wt%, which means that 95% of the NaCl in the sample is assumed to have melted, and the remainder was consumed with slight evaporation from the sample surface. The latent-heat-storage density of NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC:  $267\ \text{J/g}$  was higher than conventional ceramics/PCM composite [5,6,10], and had great potential as a heat-storage ball in a high temperature range.

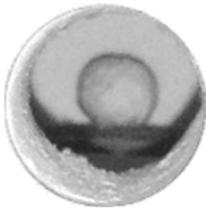
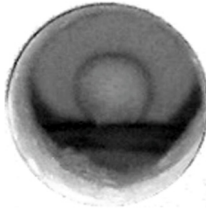
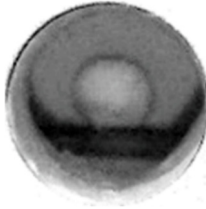
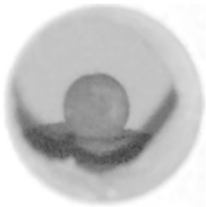
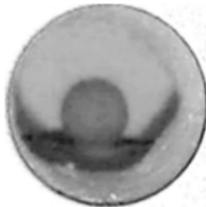
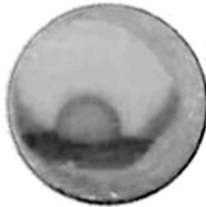
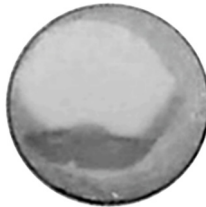


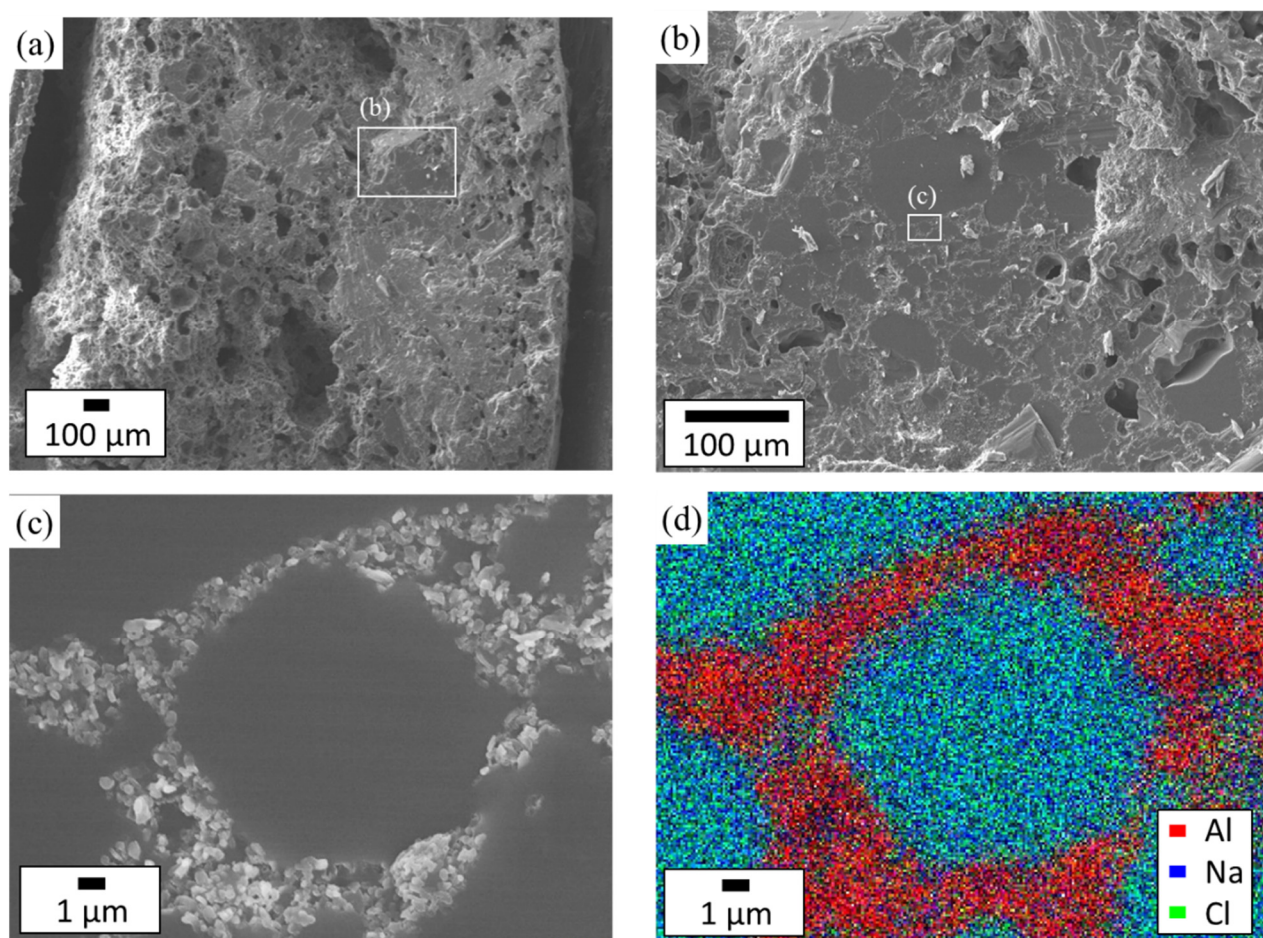
**Figure 3.** (a–c) SEM images and (d) element mapping image of position (c) using EDS of the cutting face of NaCl(80)/ $\text{Al}_2\text{O}_3$ (20)-PC ball before heating.



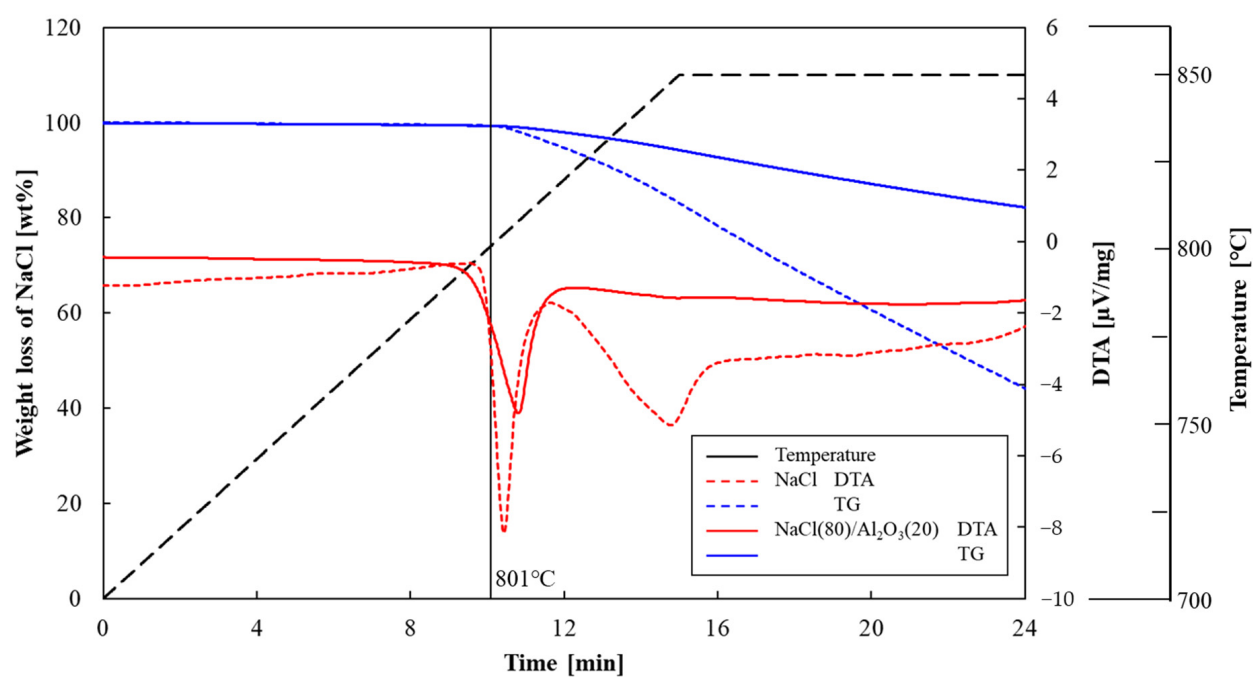
**Figure 4.** The height-change rate of NaCl/Al<sub>2</sub>O<sub>3</sub>-PC ball and NaCl ball, and heating behavior of the inside of NaCl/Al<sub>2</sub>O<sub>3</sub>-PC ball during heating at 850 °C.

**Table 1.** The shape change of NaCl/Al<sub>2</sub>O<sub>3</sub>-PC ball and NaCl ball at each temperature in furnace in Figure 4.

|                                                  | 640 °C                                                                              | 801 °C                                                                              | 850 °C                                                                               | 850 °C-10 min                                                                         |
|--------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| NaCl(80)/<br>Al <sub>2</sub> O <sub>3</sub> (20) |  |  |  |  |
| NaCl                                             |  |  |  |  |



**Figure 5.** (a–c) SEM images and (d) EDS images of the cutting face of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball after heating at 850 °C for 10 min.

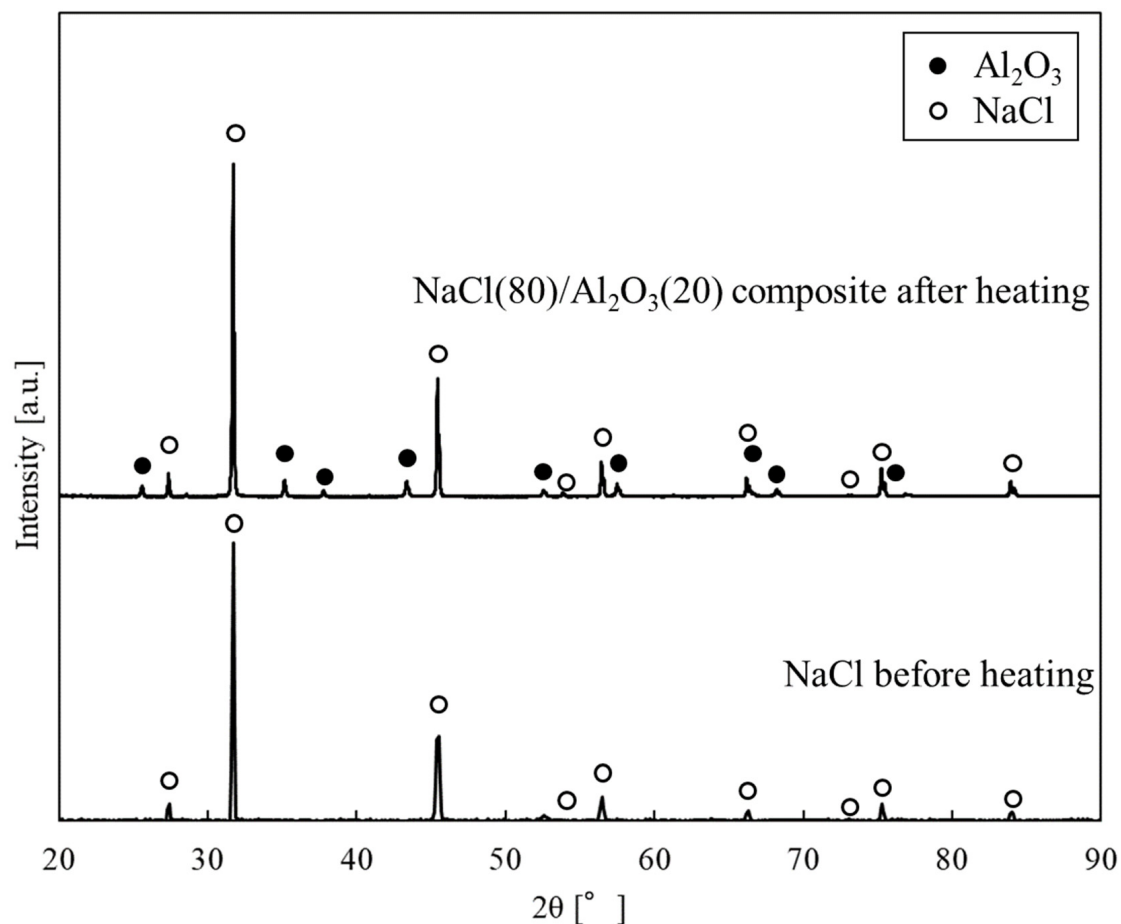


**Figure 6.** TG-TDA results of NaCl and NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC.

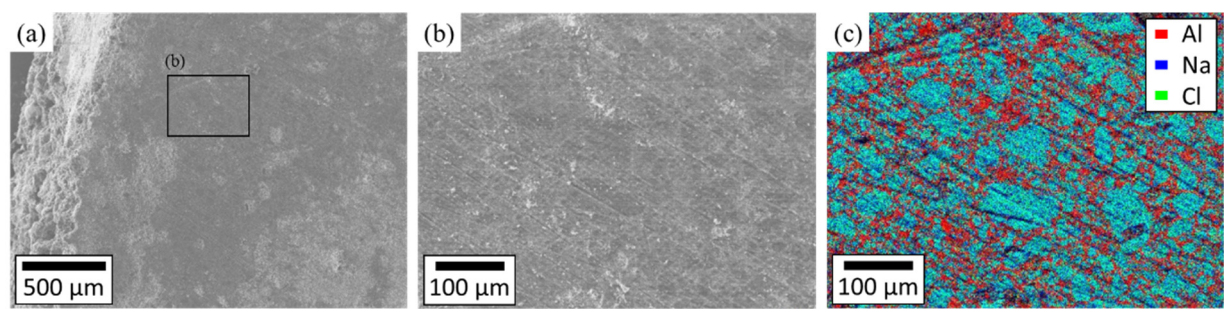


### 3.2. The Mechanism of the Shape Retention of NaCl/Al<sub>2</sub>O<sub>3</sub> PC Ball

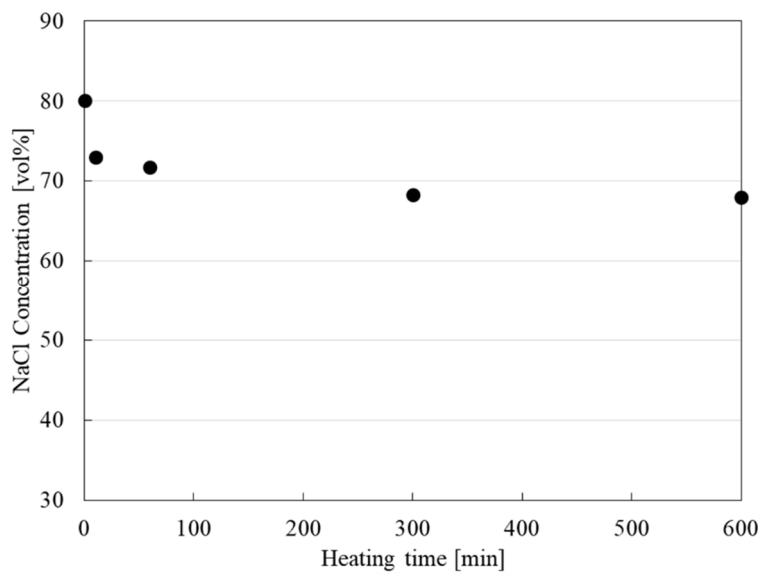
The XRD pattern of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC ball after heating at 850 °C for 10 h and NaCl powder before heating were shown in Figure 7. From the XRD pattern in Figure 7, only Al<sub>2</sub>O<sub>3</sub> and NaCl phase were shown after heating and the other reaction compounds were not confirmed. Comparison of XRD patterns before and after heating of NaCl shows no shift in peaks and a slight decrease in crystallite size calculated from Scherrer's equation at 105.5 nm and 83.9 nm. Thus, NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC ball have high chemical stability because Al<sub>2</sub>O<sub>3</sub> micro particles did not react with or dissolve in molten NaCl. And the gel like network structure of Al<sub>2</sub>O<sub>3</sub> particles containing NaCl phase was confirmed over a wide area as shown in Figure 8. It could be said that the Al<sub>2</sub>O<sub>3</sub> network structure is an important factor for maintaining the shape stably even in the molten NaCl state. The weight change of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC ball remains stable after almost 5 h in Figure 9. It is considered that the weight decreases in initial 1 h was because only outermost molten NaCl leak to outside or evaporated. And the surface structure of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball after heating for 5 h was shown in Figure 10. There are many large pores in the surface and Al<sub>2</sub>O<sub>3</sub> network structure. The volume fraction of NaCl calculated from EDS result was less than average value of 68 vol%. There was volume distribution of NaCl and, as the Al<sub>2</sub>O<sub>3</sub> concentration increases in the shell part, the viscosity becomes higher than in the inside, which is considered to be due to the shape retention. The gel like network structure by the self-assembly of Al<sub>2</sub>O<sub>3</sub> micro particles in molten NaCl was effective to prevent the leak of molten NaCl.



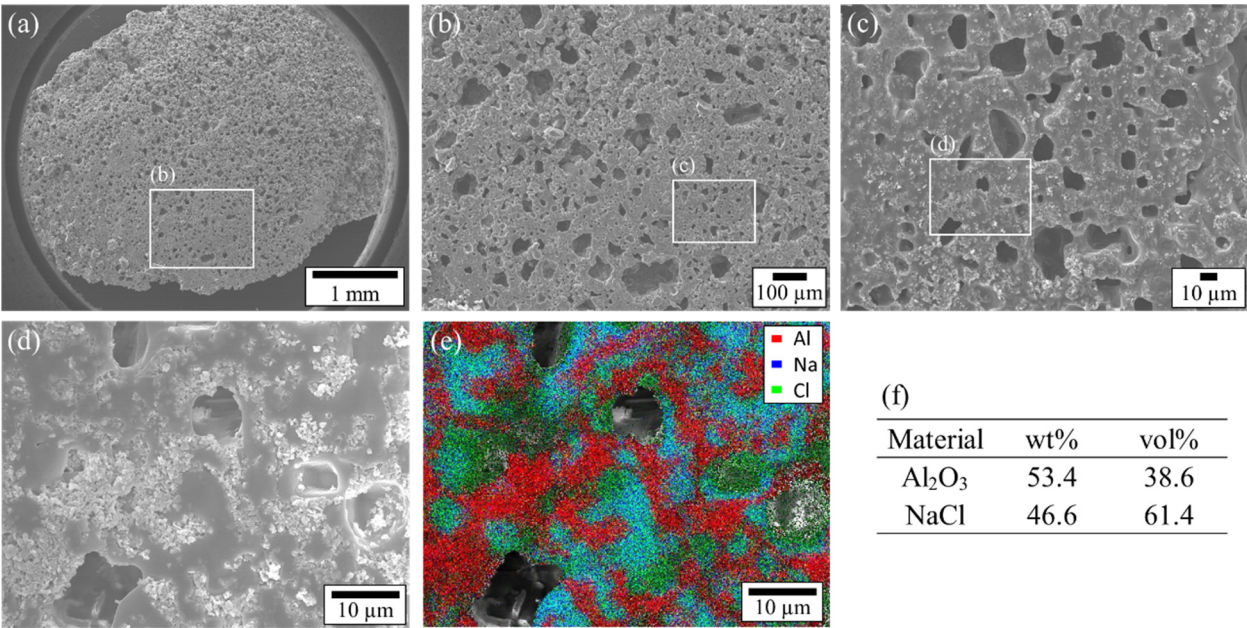
**Figure 7.** XRD pattern of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball after heating at 850 °C for 10 h and NaCl powder before heating.



**Figure 8.** (a,b) SEM images and (c) EDS mapping image of (b) of the cutting face of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball after heating at 850 °C for 10 h.



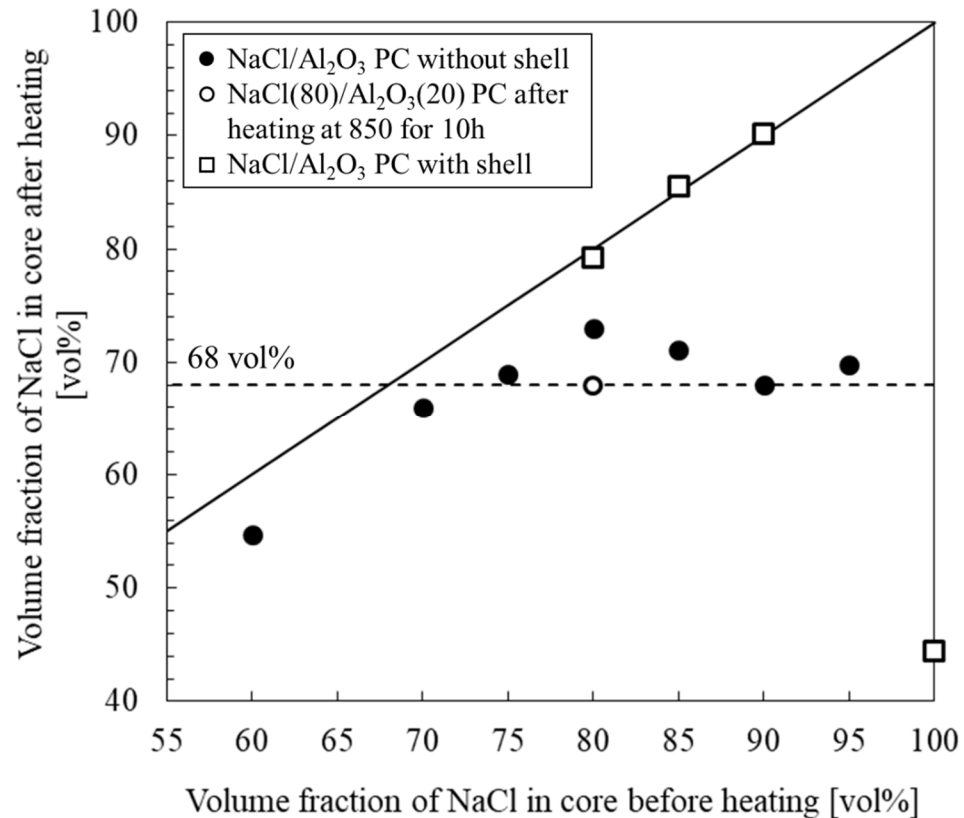
**Figure 9.** The volume fraction of NaCl after heating at 850 with different heating time.



**Figure 10.** (a–d) SEM images and (e) EDS mapping image, (f) concentration of NaCl and Al<sub>2</sub>O<sub>3</sub> of the surface of NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20)-PC ball after heating at 850 °C for 5 h.

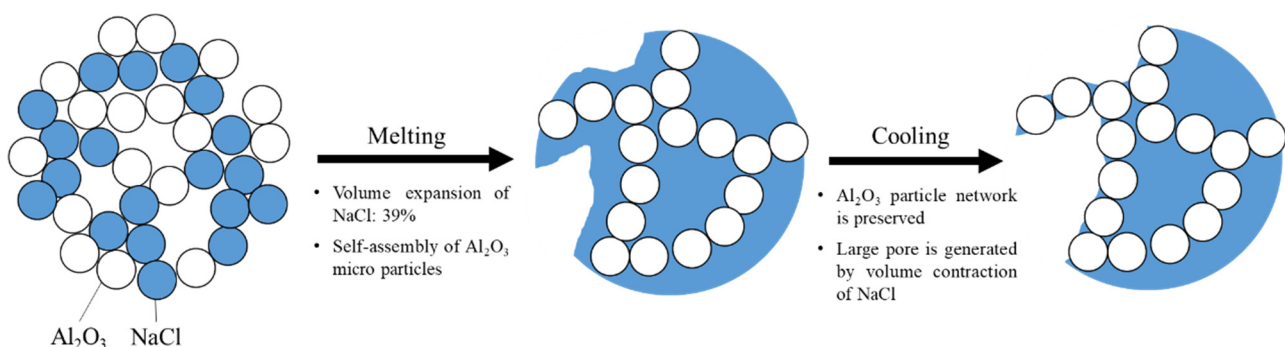


The volume fraction of NaCl/ $\text{Al}_2\text{O}_3$ -PC with and without the SiC cement shell (thickness of shell: around 2 mm) before and after heating at 850 °C were shown in Figure 11. The decrease of the NaCl volume fraction in PC within the range of 60–80 vol% is the only constant rate and is near to the ideal dotted line. However, in the range of more than 80 vol%, the weight decrease was increased with the increase of the initial volume fraction of NaCl, and the value after heating reached stability at around 68 vol%. It is suggested that the shape is maintained through increasing the viscosity of molten NaCl due to the  $\text{Al}_2\text{O}_3$  network structure. When the  $\text{Al}_2\text{O}_3$  concentration is less than 20 vol%, the excess molten NaCl leaked, since the volume of the molten NaCl phase is too much for the  $\text{Al}_2\text{O}_3$  network structure. The volume fraction after heating for 10 h in the case of 80 vol% NaCl also reached 68 vol%. It is suggested that the optimum concentration of NaCl for keeping the NaCl/ $\text{Al}_2\text{O}_3$  network structure is around 68 vol%. However, in the encapsulated sample, the weight loss was almost zero at any volume fraction of NaCl, which was in good agreement with the theoretical line. However, when the volume fraction of NaCl was 100%, more than half of the molten NaCl leaked out, and it is suggested that the composite structure with the  $\text{Al}_2\text{O}_3$  micro particles suppresses the leakage of molten NaCl. It is suggested that the shell made with SiC castable cement just prevented the leak and the evaporation of molten NaCl exiting the outermost layer of the NaCl/ $\text{Al}_2\text{O}_3$  PC ball. The NaCl/ $\text{Al}_2\text{O}_3$  powder-composite structure was quite effective in enabling stable encapsulation of NaCl as the PCM thermal storage material. In this study, NaCl concentrations as high as 80–90% were achieved when SiC castables were used as the shell material, compared to 65–70% in the conventional research about the composite of inorganic PCM and ceramic media, which is the  $\text{Al}_2\text{O}_3$ -NaCl (35–65 vol%) composite fabricated using the CSP [21], encapsulated PCM (35 vol%) [25], and PCM-impregnated composites in porous ceramics (75 vol%) [26]. Moreover, in terms of the fabrication method, this method is simpler than conventional methods because it can be fabricated at ambient pressure and temperature.

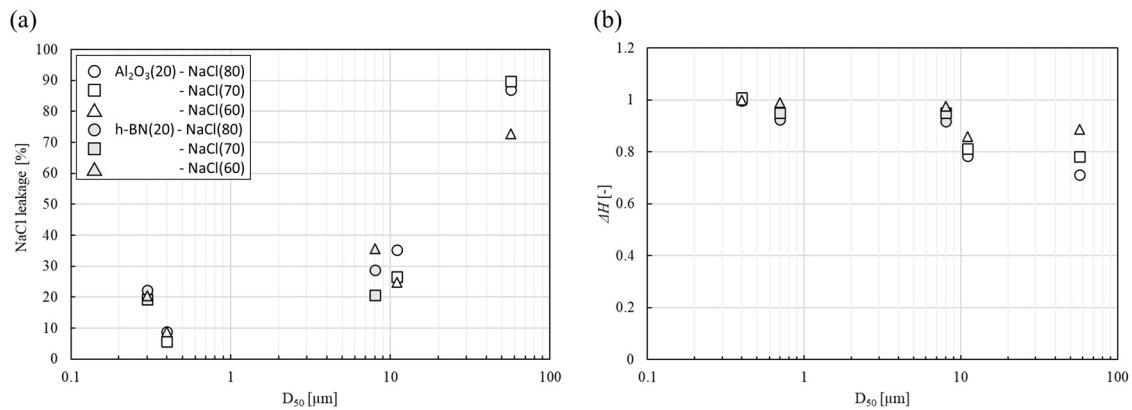


**Figure 11.** The volume fraction of NaCl after heating at 850 °C for 10 min and 10 h, before heating NaCl/ $\text{Al}_2\text{O}_3$ -PC and CS (core–shell structure).

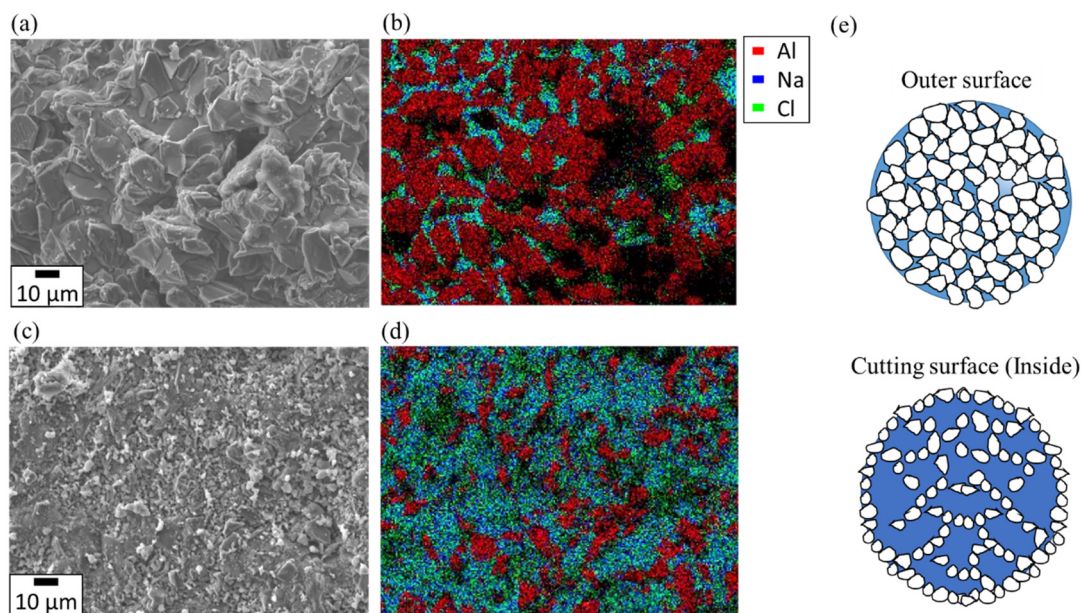
The schematics of the microstructure of NaCl/ $\text{Al}_2\text{O}_3$  PC during melting and cooling processes are shown in Figure 12. When the temperature reaches above the melting point of NaCl, the liquid NaCl phase is wet with the  $\text{Al}_2\text{O}_3$  micro particles, and at the same time the  $\text{Al}_2\text{O}_3$  micro particles aggregate in a network structure. The details of the reasons why the gel-like network of  $\text{Al}_2\text{O}_3$  particles form are currently still unclear. However, the formation of the reaction compounds were not formed even from XRD patterns, and the wettability of the molten NaCl was very good against the  $\text{Al}_2\text{O}_3$  material, so it is considered that the molten NaCl enters between the  $\text{Al}_2\text{O}_3$  particles and is connected with the liquid-bridging force. Matthew et al. have reported Pickering emulsion gels, which are the network structure of silica micro particles and the interface of an oil and water phase, formed using droplet bridging [27]. In the case of the mixed phases of molten NaCl,  $\text{Al}_2\text{O}_3$  micro particles, and pores, it is assumed that the  $\text{Al}_2\text{O}_3$  micro particles self-assemble into the interface of the molten NaCl phase and vapor phase. When the temperature decreases under the melting point of NaCl, a large pore was generated from the volume contraction from the phase change of NaCl. But, the shape of the NaCl/ $\text{Al}_2\text{O}_3$  PC ball appeared to be preserved because the  $\text{Al}_2\text{O}_3$  network structure was preserved. The effect of particle size and wettability on the leakage of molten NaCl and  $\Delta H$  after heating at 850 °C for 10 min is shown in Figure 13. In the case of the NaCl/ $\text{Al}_2\text{O}_3$  composite, the leakage of NaCl increased with the increase of the diameter of the particles. And, the leakage reaches 30% at  $D_{50} = 11.9 \mu\text{m}$  of  $\text{Al}_2\text{O}_3$ , and then it increased dramatically to more than 70% at  $D_{50} = 58.6 \mu\text{m}$  of  $\text{Al}_2\text{O}_3$ . Molten NaCl in NaCl/ $\text{Al}_2\text{O}_3$  ( $D_{50} = 58.6 \mu\text{m}$ ) composite could not be retained in each initial NaCl concentration. In the case of the NaCl(80)/ $\text{Al}_2\text{O}_3$ (20) composite using  $D_{50} = 11.9 \mu\text{m}$ , the network structure of the  $\text{Al}_2\text{O}_3$  particle is similar to that of NaCl(80)/ $\text{Al}_2\text{O}_3$ (20) using  $D_{50} = 0.44 \mu\text{m}$ , which is observed inside the sample as shown in Figure 14c,d. The micro structure of the outside surface showed an increase in the volume friction of  $\text{Al}_2\text{O}_3$  particles as observed in NaCl(80)/ $\text{Al}_2\text{O}_3$ (20) using  $D_{50} = 0.44 \mu\text{m}$ . However, the volume friction of  $\text{Al}_2\text{O}_3$  and NaCl in Figure 14d was 70.4:29.6, which was calculated using EDS analysis, which is much higher than in NaCl(80)/ $\text{Al}_2\text{O}_3$ (20) using  $D_{50} = 0.44 \mu\text{m}$  (Figure 10f). The internal volume friction of  $\text{Al}_2\text{O}_3$  and NaCl was 27.4:72.6, which is very similar to that of NaCl(80)/ $\text{Al}_2\text{O}_3$ (20) using  $D_{50} = 0.44 \mu\text{m}$  ( $\text{Al}_2\text{O}_3$ :NaCl = 27.1:72.9 from Figure 10) treated under the same conditions. This means that in the case of  $D_{50} = 11.9 \mu\text{m}$ , the leakage of molten NaCl is due to the fact that the evaporation of molten NaCl is more pronounced only on the outside, where it comes into contact with the outside air, and molten NaCl is retained in the interior where a particle network structure is formed, as in the case of  $0.44 \mu\text{m}$ . The shape-retention property of the powder-composite ball decreased with the increase of  $D_{50}$  of ceramics powder, but even at  $D_{50} = 57 \mu\text{m}$ ,  $\Delta H = 88\%$ , suggesting that shape retention is possible at high temperatures even with large levels of NaCl leakage. The lower the initial NaCl concentration, the better the shape retention, suggesting that the network structure necessary for shape retention at high temperatures can be formed when the alumina concentration is around 40 vol%.



**Figure 12.** Schematics of the microstructure of inorganic salt PCM and ceramic micro particles during melting and cooling processes.



**Figure 13.** (a) NaCl leakage and (b)  $\Delta H$  after heating at 850 °C for 10 min with different diameter of  $\text{Al}_2\text{O}_3$  and h-BN particles and initial volume fraction of NaCl.



**Figure 14.** SEM and element mapping images of (a,b) outer surface and (c,d) cutting surface of NaCl/ $\text{Al}_2\text{O}_3$  ( $D_{50} = 11.9 \mu\text{m}$ )-PC ball after heating at 850 °C for 10 min.

On the other hand, in the case of h-BN powder with poorer wettability to molten NaCl (Contact angles  $\theta = 77$  deg) than  $\text{Al}_2\text{O}_3$  ( $\theta = 0$  deg) [11], more than twice as much leakage was observed at  $D_{50} = 0.7 \mu\text{m}$  compared to the case with  $D_{50} = 0.44 \mu\text{m}$  of  $\text{Al}_2\text{O}_3$  particles, which is considered to be an effect of wettability to molten salt. However, when the particle size of h-BN was about  $D_{50} = 11 \mu\text{m}$ , there was almost no difference in the NaCl leakage amount with that of  $\text{Al}_2\text{O}_3$ . From the above, the retention of molten NaCl in powder composites with NaCl and ceramic particles is considered to be more influenced by the particle size than by the wettability of the material. The shape retention in Figure 13b also shows the same trend as in the case of  $\text{Al}_2\text{O}_3$ , indicating that the wettability of the particle has no relationship to the formation of particle network structures in molten salt, and particle size has a significant effect, probably due to cohesive forces such as the liquid-bridging force or van der Waals force. Therefore, this technique is considered to be capable of fabricating powder-composite PCM regardless of the kind of particles. It should be considered that it is an extremely innovative technique for the application to high-temperature and high-stability PCM thermal-storage material with a fabrication process at ambient pressure and temperature. As for the influence of ceramic particles on the composites, various studies [15,16] have reported improved heat transfer and specific heat capacity, and the formation of a network structure of ceramic particles on an inorganic



salt PCM material which is expected to contribute to heat transfer in the same way as in this study.

#### 4. Conclusions

A novel highly concentrated inorganic PCM (NaCl)/Al<sub>2</sub>O<sub>3</sub> powder composite as an encapsulated PCM core, which retained its shape during melting at a high temperature, was developed. The gel-like network structure composed of the self-assembly of Al<sub>2</sub>O<sub>3</sub> particles in molten NaCl was key to keeping molten NaCl and preventing its shape from collapsing. An NaCl/Al<sub>2</sub>O<sub>3</sub> powder-composite structure with a high NaCl concentration of 68 vol% showed high stability even after heating at 850 °C for 10 h without encapsulation. The latent-heat-storage density of the NaCl(80)/Al<sub>2</sub>O<sub>3</sub>(20) PC sample was 267 J/g which was calculated from the TG-DTA results. The mechanism of NaCl-leakage suppression and its high shape retention at high temperatures is largely dependent on the particle size, with little effect on the wettability of the composite particles. The formation mechanism of the gel-like network is assumed to be due to the aggregation of ceramic particles with the liquid-bridging force which is generated between Al<sub>2</sub>O<sub>3</sub> particles via the molten NaCl or the formation of Pickering emulsion gel. Through coating NaCl/Al<sub>2</sub>O<sub>3</sub> PC with a SiC catalytic cement shell, molten NaCl leakage could be suppressed almost completely, enabling stable encapsulation. A PCM-composite structure with a gel structure from the self-assembly of Al<sub>2</sub>O<sub>3</sub> micro particles in a molten NaCl phase is an innovative idea for a PCM heat-storage material for high temperatures.

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