Encapsulated Copper-Based Phase-Change Materials for High-Temperature Heat Storage

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ABSTRACT: In this study, a copper-based capsule, encapsulated by a black alumina shell using a simple method, was developed for high-temperature heat storage over 1000 °C. The shell was filled with copper beads (diameter = ∼3 mm), the copper–aluminum (Cu–Al) atomized powder (particle size = 150 μm) was filled in the gap, and then it was heat-treated. This eventually formed a high-density, aluminum-rich network around the Cu beads in the shell. Morphological observations indicated that the corrosion of copper oxide (CuO) on the alumina shell was significantly reduced by mixing Al with Cu. When heat-treated in air at 1100 °C, Cu became CuO, which reacted with Al2O3 to form a new compound, CuAl2O4. Owing to this two-step reaction, the area around the hole provided at the top of the spherical shell gets sealed, thereby suppressing the flow of oxygen into the shell (self-sealing function). The mechanism of in situ sealing was detected using X-ray diffraction and scanning electron microscopy analyses. The Cu–(5–10%) Al capsule could endure a 400 h air exposure test at 1100 °C without leakage or cracking. A low weight increase ratio of 3.5% after the exposure revealed good oxidation resistance of the capsule, whereas the slight damage load change of the capsule after the exposure showed good mechanical stability. The results concluded that a Cu–(5–10%) Al capsule for high-temperature heat storage applications above 1000 °C can be fabricated by a simple process, and it demonstrates excellent durability during the long-term air exposure test. The data obtained in this study can be used as a reference for the design of packed beds in the future.

1. INTRODUCTION

Currently, the effective utilization of thermal energy and reduction of CO2 emissions in the use of fossil fuels are becoming critical areas of concern for many countries around the world. With regard to renewable energy sources, solar energy is considered a promising alternative to fossil fuels, and it currently accounts for a large proportion of renewable energy basket.1 However, solar energy is not available at night, and there is a time mismatch between solar energy supply and electricity demand.2 As a result, the use of thermal energy storage (TES) systems with an oversized solar field is being pursued to optimize the economics and dispatchability of solar thermal concentrating solar power (CSP) plants in many countries.3 When surplus electricity is generated by a CSP plant, solar energy is temporarily stored as heat. Subsequently, when the demand for electricity increases, the stored heat is converted back into electricity. In addition to solar energy, large sources of thermal energy, such as waste heat from power plants, are not effectively utilized. In contrast, 18% of the energy consumed in Japan is attributed to industrial furnaces.4 Therefore, improving the efficiency of industrial furnaces has become increasingly important to save energy and reduce CO2 emissions. With regard to industrial manufacturing processes, waste heat is generally discharged into the ambient atmosphere with exhaust gas. This indicates that the recovery efficiency for unstable and intermittent waste heat needs to be improved. In the past, many technologies have been developed to recover waste heat from exhausted gas. For instance, combustion technology that utilizes heat storage materials to recycle the heat generated by burners was proposed to enhance the efficiency of industrial furnaces; these regenerative burners have been widely applied in Europe and United States.5 Therefore, to solve the temporal and spatial mismatch of supply and utilization of heat and improve the utilization efficiency of thermal energy, a compact high-temperature TES system is essential for the effective use of solar energy and exhaust heat.6

Depending on their heat storage mechanism, heat storage materials are divided into sensible, latent, and chemical heat storage materials.6 Sensible heat storage materials have a lower...
storage capacity than both latent and chemical heat storage materials; therefore, their systems are generally very large. Chemical heat storage materials use reaction heat and store thermal energy into stable chemical substances. Although they have a high heat storage density, it is difficult to control the reaction conditions, and special reactors are often required. Materials that use latent heat are known as phase-change heat storage materials. The phase-change materials (PCMs) used as cooling media can absorb/release latent heat during the melting/solidifying process to achieve a relatively constant temperature. Compared with conventional sensible heat storage materials, latent heat PCMs can store heat at a high density in a small temperature range. Therefore, PCMs are widely used in various TES systems.

PCMs are typically divided into three main types: inorganic, organic, and metals and are selected with corresponding melting points depending on the operating temperature. The most common application of PCMs is in the form of a packed-bed type system to store heat from high-temperature fluids because of the high heat-transfer area between the storage (spheres of PCMs) and the heat-transfer fluid. To avoid direct contact between the heat-exchange medium gas and the heat storage material, the material is encapsulated into an encapsulated heat storage capsule (EPCM). Encapsulation not only increases the heat-transfer area but also prevents the leakage of PCMs. The core materials are generally selected based on their melting point (which needs to be close to the operating temperature), whereas the shell materials are chosen according to their corrosion resistance, thermophysical properties, and mechanical properties. A large number of heat storage capsules are packed into the heat-exchange tank, and the gas is treated as a medium to pick up and exchange heat through the interval between each capsule.

Presently, high-temperature waste heat (from 500 °C to more than 1000 °C) is generated in many processes in the metal production and mineral processing sectors. To further increase the heat utilization in such processes, it is necessary to develop a higher temperature PCM heat storage technology. However, waste heat above 1000 °C is still difficult to recycle efficiently via an EPCM because of the extremely high temperature.

Generally, PCMs used at high temperatures include molten salts such as alkali metal nitrates and metals with high melting points. When compared with molten salts, which generally suffer from inherently low thermal conductivity, metal materials are more suitable as high-temperature PCMs owing to their ultra-high conductivity and satisfactory heat fusion.

Cu is regarded as one of the most promising PCMs for high-temperature heat storage because of its high melting point (>1000 °C), high thermal conductivity, and latent heat (208.7 kJ/kg). In recent times, Cu-based macro-PCMs for ultra-high temperatures (over 1000 °C) have been studied extensively.

Akiyama et al. encapsulated copper balls (3 mm in diameter) by a nickel shell using an electroplating method. In this case, carbon or ruthenium was inserted as an inhibition layer. As a result, the shell and its inactive layer remain in the shape of an EPCM during the heating process. However, the nonuniform distribution of carbon shows a risk of leakage.

Kisi et al. try to develop a Cu–Fe system which can be utilized over 1000 °C by a powder metallurgy process. The miscibility gap binary alloy systems of Fe–Cu could live up to expectations upon short-term testing. However, only the material properties have been tested in this study. The encapsulation method and the durability of the material still need to be studied and confirmed.

Zhang et al. selected copper balls (diameter = 2 mm) as PCMs to encapsulate a thick chromium–nickel bilayer via a novel chromium periodic-barrel electroplating method and a nickel barrel-plating method. The results demonstrated the excellent oxidation resistance of the capsules and the good stability between Cu and chromium–nickel layers, even after long-term charge–discharge cycles. However, the chromium periodic-barrel electroplating process is complex from the point of view of fabrication compared with the mechanically encapsulated method. Although this method is suitable for encapsulating small-sized PCMs, supercooling and the small path of heat-transfer fluids are still possible to limit the efficient application of a small-sized EPCM.

To encapsulate macro-PCMs with a high melting point via a physical method, Wickramaratne et al. sintered hemispherical ceramic caps and joined them to encapsulate the PCMs. The fabricated capsules survived more than 150 thermal cycles without any degradation in their thermophysical properties. However, this complex manufacturing process limits its industrial application. It also requires an additional sealant as well as sealing temperature controls.

Nomura et al. proposed a capsule with a Cu core and two parts of a cylindrical alumina cup. However, owing to the cylindrical shape of the shell, the edge of the capsule suffers from a concentrated force during the expansion process. In addition, Cu was sealed under a nitrogen atmosphere. Considering the reactivity of CuO and alumina, the practicality of the product needs to be proven. To date, there have been few reports on successful high-temperature Cu-based macro-PCMs.

The drawbacks that limit the practical application of Cu-based EPCMs are as follows: (1) CuO shows strong reactivity with ceramic/metallic shells, which corrode the shell and affect the performance and durability. (2) Shells are complicated to manufacture, and the inner metal needs to be fabricated as a sphere to fill. (3) The void space or the gap in a large-scale capsule decreases the heat storage density.

To solve these problems, a Cu-based high-temperature EPCM was developed with a simple manufacturing process, high packing ratio, high durability, and an in situ seal. A thin-walled spherical shell using black alumina was fabricated, and the Cu–(5–10%) Al alloy was filled as the core. The developed EPCM shows the following advantages over conventional products: (1) without an interval between the core and the shell, the amount of PCM increases, and the heat storage density of a single capsule improves. (2) At the inlet of the capsule, where the Cu–(5–10%) Al alloy can get in touch with oxygen, Cu and Al are expected to react with oxygen when the alloy is heated to 1200 °C and seal the inlet to prevent the alloy from leakage, which makes it possible to simplify the fabrication process. (3) Adding Al to the core, it can be oxidized and reacted with CuO to inhibit the corrosion of CuO to the alumina shell at the boundary between the core and the shell. In situ sealing also prevents oxygen from entering the core and restricts the oxidation reaction in the EPCM. The Cu–(5–10%) Al EPCM shows the chemical and mechanical stability in ambient air over 1000 °C during long-term cycling, which proves its potential for high-temperature heat recovery applications.
In this study, the mechanism of in situ sealing occurring on the Cu–(5–10%) Al EPCM was hypothesized, which was subsequently confirmed based on morphological observations and X-ray diffraction (XRD). The durability of the sample was evaluated via a long-term air exposure test at a high temperature for the Cu–(5–10%) Al EPCM. The chemical and mechanical stability was also reported in this work using the oxidation ratio, heat-transfer performance, and damage load.

2. EXPERIMENTAL METHODS

2.1. Preparation of the Specimen. 2.1.1. Shell. Powders weighing 2 wt % Cr₂O₃, 2 wt % MnO₂, 2 wt % Fe₃O₄, 2 wt % Co₃O₄, and 92 wt % Al₂O₃; distilled water of almost the same load.

The obtained slurry was stirred again.

Further, approximately 1% of an antifoaming material and an acrylic water-soluble binder were added to the obtained slurry, and the mixture was stirred again, and then sintered in air at 1600 °C for 2 h. The outer diameter of the spherical cavity with an inner diameter of 28 mm and left for a predetermined time; water was absorbed by the gypsum mold to obtain a spherical shell-shaped molded product.

The slurry thus obtained was injected into a gypsum mold provided with a spherical cavity with an inner diameter of φ = 28 mm and left for a predetermined time; water was absorbed by the gypsum mold to obtain a spherical shell-shaped molded product with a wall thickness of approximately 2.5 mm.

The obtained molded product was dried in a drying oven and then sintered in air at 1600 °C for 2 h. The outer diameter of the sintered body was approximately 25 mm, and the wall thickness was nonuniform but approximately 2 mm. The top contained a hole of approximately 5 mm in diameter, as shown in Figure 1.

Figure 1. Scale of the shell.

2.2. Core and Its Encapsulation in the Shell. In addition to the high density, another reason for adopting such an arrangement is the formation of an aluminum-rich network phase around pure Cu, which is expected to suppress Cu oxidation even with a small amount of Al. First, the alumina shell is filled with as many copper beads as possible and then the Cu–40% Al alloy powder is added until all the gaps in the shell are filled. The aluminum filling rate depends on the volume of the gap in the shell after the first filling of the copper bead. The average mass fraction of Al in the filling was varied from 5 to 10%. The inner volume of the alumina shell and the diameter of the copper bead are manufactured as per the same specifications. First, the shell is weighed and is denoted as W₁. As mentioned earlier, when the beads are filled inside the shell under vibration, they are filled in almost the same way (W₂). The mixture measurement before and after filling shows the weight of the beads filled in the shell (W₂–W₁). Next, the gaps between the beads are filled with an alloy powder of known composition under shaking and the weight (W₃) is measured. The weight of the alloy powder is calculated as W₄ = W₂–W₃. Therefore, when using Cu beads and the Cu–40% Al alloy powder, the composition of Al is 40 *W₄/(W₁–W₃). As a result, the average mass fraction of Al in the filling was varied from 5 to 10%. In addition, the change of aluminum between 5 and 10% is an error caused by production and operation, and the whole quality of the PCM does not change much. The EPCM was heated at 1200 °C for 2 h in ambient air. The raw materials of the core and the shell are listed in Table 1. The fabrication process of the EPCM is illustrated in Figure 2 as a flow chart.

To test the durability of the EPCM, the capsule was exposed to air for 200 h at a temperature of 1100 °C using an electric furnace. The samples were heated to this temperature and cooled to room temperature seven times over a period of 200 h. In addition to this test, seven new samples were prepared, and an exposure test at 1100 °C for up to 400 h was added. The mass change of the capsule after each cycle was recorded to estimate the oxidation ratio of the EPCM. The melting point of pure Cu is 1083 °C, and the temperature of this exposure test was set to a value higher than the melting point.

2.3. Evaluation Method. 2.3.1. Leakage Test. For optimizing the filling method and composition of core materials, four capsules were filled by different methods and compositions. In order to compare with the development of the Cu–(5–10%) EPCM (Cu beads; Cu–40% Al powder), (A) φ3 beads, (B) Cu powder, and (C) Cu–Al atomized products were selected as the core copper, and each of these was filled inside the alumina ceramic shell until it was full. In that state, they were heated in air at 1200 °C for 2 h. After melting, the appearance of the capsules was observed to ensure if there is no leakage in the high-temperature heat storage process.

2.3.2. Morphological Observations. The cross sections of the spherical EPCM samples were observed after heating at 1200 °C via X-ray microtomography (SKYSCAN, BRUKER).

Table 1. Raw Materials of the Core and Shell

| material | P/powder | maker | code | content (wt %) | average diameter, mm |
|----------|----------|-------|------|----------------|---------------------|
| black alumina shell | Al₂O₃(P) | Nippon Light Metal Co., Ltd. | SA32 | 92 | 1 |
| Cr₂O₃(P) | Kojundo Chemical. Laboratory Co., Ltd. | 5180872 | 2 | 1 |
| MnO₂(P) | Kojundo Chemical. Laboratory Co., Ltd. | 5180973 | 2 | 1 |
| Fe₃O₄(P) | Kojundo Chemical. Laboratory Co., Ltd. | 5180874 | 2 | 1 |
| Co₃O₄(P) | Kojundo Chemical. Laboratory Co., Ltd. | 5180871 | 2 | 1 |
| core | atomized Cu–Al (P) | Hikari Material Industry Co., Ltd. | Cu–40Al | Cu 60% Al 40% | 150 |
| Cu (B) | Sansyo | 44–2225 | pure Cu | 3 |
Then, the EPCM was cut into half, and the morphology of the interval as well as the inlet was observed using a scanning electron microscope (S-4300, Hitachi, Japan), whereas the elemental distribution of the sample components was analyzed via energy-dispersive X-ray spectroscopy (EDX; JEOL, JED-2300T & Gatan, GIF quantum ER). In addition, XRD was used to analyze the phase composition near the inlet area.

2.3.3. Structural Characterization. The seal material sample was taken from the capsule and crushed into powder. The seal material sample was investigated using XRD (SmartLab, Rigaku) with Cu Kα radiation (λ = 0.15418 nm and 40 kV to 25 mA). Crystalline phases were analyzed using a PHXL2 (Rigaku Data Analysis Software).

2.3.4. Oxidation Ratio Test. A 200 h exposure test was performed on a Cu−5.40% Al capsule in an air atmosphere at 1100 °C. During the exposure test, heating was performed with the inlet facing down. The experimental process was divided into seven steps. The mass changes during the test were measured to estimate the oxidation ratio of the EPCM. In order to obtain longer antioxidant performance and to evaluate the reproducibility of experimental results, seven similar capsule samples [Cu−(5−10 wt %)Al] were prepared using the same method, and the weight increasing ratio of the samples within 400 h was tested under the same experimental conditions.

2.3.5. Heat-Transfer Test. A heat-transfer test was performed on the EPCM before and after 200 h of exposure to evaluate the heat-transfer performance and to clarify the chemical and structural stability after long-term air exposure. The capsules were heated using an electronic heater surrounded by an insulator. In this experiment, the heater was set to 773 K. A hole with a diameter of 1 mm and a depth of 12.5 mm was drilled at the inlet of the EPCM by machining to set the tip of the thermocouples in the center of the ball and then recording the temperature behavior of the ball center. For comparison, a conventional solid spherical heat storage body made of white alumina (o = 25) was also used for the measurements. In addition, the substance in black alumina with the same structure was used for comparison. A hole of Φ = 1 mm was drilled from the surface to a depth of 1, 3, 5, and 12.5 mm (center), and thermocouples (Φ = 0.5 mm) were used to analyze the temperature distribution.

2.3.6. Mechanical Strength Test. The damage loads of the EPCM sample after heating for 2 and 200 h were measured using a tension/compression tester (Imada Seisakusho Co., Ltd; SDW-9103-R3) to evaluate the durability of the EPCM and compare the mechanical property changes after the exposure test. In addition, a hollow black alumina shell with a diameter of 25 mm and a thickness of 2 mm was prepared to compare the mechanical properties.

3. RESULTS AND DISCUSSION

3.1. Leakage Test. Figure 3 shows the appearance before and after exposure to the atmosphere. In A and B, the molten core material leaks severely from the inlet to the outside and reacts with the alumina plate, which is asetter, to darken. In Cu−30% Al, the leakage was alleviated, but it was still observed that the leakage occurred from the top part. The reaction generated in this way, and its meaning will be described later. If the same experiment is performed using atomized powder with a different Al composition, leakage can be suppressed as the amount of Al increases. However, as shown in (C), leakage...
could not be suppressed even with 30% Al using atomized powder alone.

On the other hand, (D) is a sample in which 77.3% of the entire core is charged using pure Cu beads, and then 12.7% of Cu−40Al atomized powder is filled into the rest space. The average composition of the sample was calculated as Cu−6.05Al%. On the basis of the internal volume of the shell and the average density of the Cu−6.05Al alloy, the packing ratio could be calculated as 77.3%, which was improved to about 80%. The appearance of the capsule after 2 h of heating is shown in (D). It can be found that the shell was intact, and no leakage occurred. It was confirmed that almost no leakage occurred even when exposed to the atmosphere at 1200 °C. The inlet was closely sealed by seal materials formed by the reaction.

The cross section of the capsules in leakage test is shown in Figure 4. Figure 4A,B shows that some of the copper leaked due to the volume change of copper during melting and flowed out of the unsealed inlet, forming a cavity at the top. In addition, regardless of the copper powder or bead, the upper phase is severely oxidized and cannot be utilized as a latent heat storage material. Figure 4C shows that the capsule filled with the Cu−30% Al alloy powder failed to dissolve into an alloy due to surface oxidation. On the contrary, only the Cu−6.05% Al sample in Figure 4D forms the reactants that seal the inlet. Besides, no leakage or intense oxidation zone was observed like others.

After that, a series of studies were conducted using the EPCM with a mixture of beads and powder as the core material. The results are described hereinafter.

3.2. Morphological Observations. 3.2.1. Inner Appearance of the EPCM. The internal morphology of the capsule was observed using X-ray microtomography. The perspective image of the Cu−5.18% Al EPCM, shown in Figure 5A, was scanned via an X-ray microtomograph. There were no distinct holes in the alloy core, and a high packing ratio and a dense internal structure were observed. After scanning, the shell of the Cu−5.18% Al EPCM was broken and is observed in Figure 5B. It was observed in the destroyed shell that the outer surface of the inner alloy core was dense without obvious holes, which is absolutely in agreement with the observations of the X-ray microtomography photo.

According to Figure 5A, the distribution of the Al phase showed a network structure and surrounded the Cu phase in the center of the core. Besides, the alloy core touched the alumina shell closely in the northern hemisphere, whereas a tiny gap with a maximum width of 0.25 mm was seen only in the southern hemisphere. As shown in Figure 6, an increase in packing ratio effectively reduces the size of the gap between the shell and the core. Due to filling with powders of different particle sizes, Al is distributed in the core with a network structure, whereas the Al distribution is more uniform and concentrated at the inlet area and boundary without copper beads. The Cu-based capsules did not leak after mixing Al with Cu. Interestingly, the inlet was sealed in situ after the heating process.

We hypothesize that the Cu−(5−10%) Al powder at the top inlet melts at 1200 °C and reacts with oxygen in air to form a Cu−Al−O layer. As the reaction progresses, the inlet is gradually sealed by the products to prevent the inner metal from contacting oxygen. Similarly, oxidation and chain reactions may have occurred at the boundary between the core material and the shell, as shown in Figure 6. As the reaction generated at the core−shell boundary, a Cu−Al−O layer also formed between the core and the shell, which avoided alumina shell corrosion by metallic oxide and restricted oxygen diffusing into core material. To validate this hypothesis, we analyzed the observation results at the boundary and the in situ seal layer, as detailed in the following sections.

3.2.2. Core−Shell Boundary Area Observations. The results in Figure 7 show that when heated in the presence of air, the core material is in close contact with the shell at the boundary. To clarify the reason for the absence of a gap structure at the boundary, Cu−5.18% Al capsules were prepared for the scanning electron microscopy (SEM) observation. The shell fragments were wrapped in resin and polished for observation. Figure 7 illustrates the cross section of the alumina shell of the capsule after 2 h of heating at 1200 °C. The SEM images show that a film with a width of 14 μm formed on the inner surface of the alumina shell. The boundary shape between the alumina shell and the film is relatively regular and clear. Based on the Cu element distribution result using EDX, few Cu elements were detected from the alumina shell, which indicates that the shell did not react with the core material because of the protection from the
The compositions of the films were analyzed as CuAl2O4 and CuO by atomic number proportion. The reason for this is that Al and Cu do not react with the aluminum oxide (Al2O3) shell, whereas the Al2O3 shell can only react with CuO. During the heating process, Al was oxidized to alumina and possibly reacted with CuO, as shown in eq 1, over 1000 °C. When the temperature exceeded 950 °C, alumina reacted with alpha alumina to form CuAl2O4.24 The metal powder filled the gap between the copper beads, and the alumina shell contains 40% Al. Increasing the Al content reduces the probability of Cu contact with the outer shell. In addition, alumina oxide generated by the powder at the boundary also has the opportunity to react with CuO. Because the Cu and Al powders were mixed very uniformly before heating, the alumina generated from the powder reacted with the CuO generated in the powder more preferentially than the alumina shell. The generated CuAl2O4 layer sealed the core materials at the boundary and avoided the reaction between CuO and the shell.

Furthermore, the CuAl2O4 layer can block the path of oxygen inside the shell and reduce the oxidation rate of the EPCM. When the Al content is up to 5.18%, a capsule without a gap can be obtained, while the corrosion of the alumina shell by CuO can be minimized.

\[
\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4
\]

(1)

The CuAl2O4 layer prevents further contact between CuO and the alumina shell and alumina from oxidation of aluminum powder, and then the Cu phase is coated by the Cu–Al–O layer and the alumina layer. As predicted in the previous section, the path of oxygen decreases because the boundary gap gradually disappears. As a result, the reaction stops, and the phases become stable in the boundary area. This result is in good agreement with the inferences in the previous section. In conclusion, mixing with Al powder reduced the reactivity of the Cu-based PCM to the alumina shell. Filling the Cu–Al powder into the interval between the Cu beads and the shell not only limits the oxygen path but also generates a buffer between the core material and the shell. As a result, the Al2O3 film prevented the corrosion of the alumina shell by CuO. In addition, the CuAl2O4 layer formation is possible to seal the interval between the core and the shell in situ with the forward reaction of (1) at the inlet area of the EPCM. The boundary in situ seal suppresses the oxidation reaction by
stopping the diffusion of oxygen from the outside into the capsule.

3.2.3. Mechanism of the In Situ Seal at the Inlet. To clarify the mechanism of the in situ seal at the inlet, the sealing layer and the boundary area near the inlet were observed and analyzed by SEM and EDX, respectively.

The surface morphology of the Cu−5.18% Al core boundary was also imaged using SEM. Figure 8 shows the micrographs and EDX results for the boundary area of the core near the inlet. The EDX results indicate that metals were oxidized at the boundary area near the inlet where it was possible to get in contact with oxygen. An alumina film was formed between the alloy core and the black alumina shell with a thickness of 200 μm. EDX analysis further revealed that the Al phase was oxidized to alumina and surrounded the Cu phase in the zone close to the film.

Further observations were carried out in the region of the Cu−Al network structure, as illustrated in Figure 8. A gray buffer phase can be clearly observed in the interval between the bright Cu phase and the black alumina phase. Using EDX analysis, the Cu−Al−O phase, which possibly consisted of CuAl2O4 or CuAlO2, formed between the Cu and alumina phases as shown in Figure 9.

This distribution pattern indicates that oxide formation is also detected at the outermost boundary of the core metal, which is in agreement with the observations of the shell. CuO, Al2O3, and CuAl2O4 were detected simultaneously at the boundary area of the core.

The seal material layer was analyzed using SEM and EDX. As shown in Figure 10, the seal material layer has a thickness of approximately 1.5 mm with a porous structure. It seems that many pores remain near the entrance. From the results of the oxidation resistance test described later, the intrusion of oxygen into the interior is small. The pores present in this porous region are likely to be closed pores. It can be seen from the EDX result of the center seal that the CuO phase is surrounded by the alumina phase, and there is a Cu phase on the periphery of the alumina phase.

Three phases interleaved with each other, and a three-phase overlapping lamination structure appeared locally. The EDS analysis results show that the three phases were CuO, CuAl2O4, and alumina, as shown in Figure 11. CuAl2O4 acted as a buffer between the dispersed alumina and the CuO phases, almost at the interface between alumina and CuO.

In addition, the XRD diffractograms of the in situ seal material of the Cu−5.18% Al EPCM after 2 h at 1200 °C heating are shown in Figure 12. The results reveal that CuAl2O4 and α-alumina were the main phases in the seal, which agrees with the EDX analysis before Figure 12. The interfaces between the phases were very neat and compact.
During heating, the Cu–Al mixed powder at the inlet was first oxidized to CuO and alumina, which eventually reacted to form CuAl₂O₄ as reaction 1.

The CuAlO₂ peak was detected, whereas the Cu₂O peak was not detected in the seal material. Therefore, the porous structure in the seal layer was possibly formed by the oxygen-releasing reaction 2 in the absence of oxygen.

\[ \text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2 \]  

(2)

The excess CuO in the case of hypoxia will continue to be absorbed by CuAl₂O₄ until each phase reaches the equilibrium and the reaction completely stopped.

Based on the results, the mechanism of in situ sealing was analyzed. Similar to the boundary seal film, Cu and Al were distributed uniformly in the powder filling at the inlet. When heated to 1200 °C, the metals react with oxygen to form alumina and CuO. According to eq 1, alumina and CuO continue to react to form CuAl₂O₄. CuAl₂O₄, which is stable and has a higher melting point than Cu and Al, does not react with alumina and may continue to react with CuO or decompose into copper aluminate under anoxic conditions. With the decrease in CuO, the reaction between CuO and alumina gradually stopped and the CuAl₂O₄ phase layer stabilized. Crossed alumina and CuAl₂O₄ phases gradually thicken, become dense at the inlet, and prevent further diffusion of oxygen into the inner metal core, resulting in a decrease in the oxygen concentration at the inlet. Finally, the oxide layer is connected into one piece, which physically isolates the PCM from the outside environment. All phases in the seal layer tend to become stable states, and the self-sealing process is completed.

### 3.3. Durability Analysis

#### 3.3.1. Oxidation Ratio

An EPCM sample with an average Al composition of 5.40% was prepared to test the oxidation ratio during long-term exposure to air at 1100 °C. The sample was heated continuously in stages for 200 h. Figure 13 shows the weight increase ratio in each heating step. It is evident that only a 3.0% weight increase was observed after the 200 h exposure. In the figure, the data indicated by the white mark are the results of holding the same sample for a predetermined time and showing the weight increase of the PCM portion at that time. This is the result of a heating test for up to 200 h using the same sample (initial test). The rate of change in weight was fast in the initial stage but then slowed down to about 3% after 200 h.

Furthermore, the black mark indicates the weight change ratio of PCM with respect to the initial weight at 1100 °C for 300 and 400 h by newly preparing seven samples by the same method separately from the above samples (additional test). The ratio of change in weight due to oxidation is about 3.5% even after 400 h, and it can be seen that the tendency is almost the same as the curve of weight change shown in the initial test. No cracks were observed in all the seven samples. From a practical point of view, the goal is to hold the weight change to 5% or less in 1000 h, and it is highly possible that this durability can be achieved from the behavior of the oxidized weight.

The specific densities of Al and alumina are 2.7 and 4.0, respectively. If all the Al that originally existed in the core changed to alumina, the weight increase would theoretically be 2.6%.

However, the weight increase was approximately 3.0% even after long-term exposure, which infers that Al was oxidized but Cu almost remained unreacted. Therefore, it is evident that Al is selectively oxidized even if oxygen invades at a high temperature to prevent the oxidation of Cu.

With the aim of demonstrating the selective oxidation, two samples of Cu–5.18% Al were prepared for observation using Cu beads and Cu–40% Al powder. One of the Cu–5.18% Al capsules was heated to 1200 °C in an Ar atmosphere, whereas another Cu–5.18% Al capsule was heated to 1200 °C in an air atmosphere. As shown in Figure 14, the core heated in the Ar atmosphere is fully oxidized, whereas the core heated in air is only partially oxidized. Figure 14 shows the cross section of Cu–5.18% Al capsules. (A) After 2 h of heating at 1200 °C in Ar and (B) after 2 h of heating at 1200 °C in air.
Atmosphere became a uniform alloy, while a network structure can be clearly found from the cross section of the core heated in air. This suggests that the appearance of the internal network structure is related to the oxidation reaction during the heating process.

In order to make the reason of low oxidation clear, further analysis was carried out for core materials using SEM and EDX. Figure 15 illustrates the cross section of the core materials with an average composition of Cu−5.18% Al.

Only a small amount of aluminum and oxygen elements was detected at the location of the copper beads. On the contrary, the distribution of aluminum and oxygen is highly consistent in the area where copper and aluminum powder particles were originally filled in the gap of the copper beads, while the oxygen element is still small in the copper enrichment area. These phenomena confirm that aluminum is indeed preferentially oxidized to alumina in the core material. In the initial stage, the inlet of the capsule is not sealed, and oxygen can enter the capsule through the gap of the filling. In this process, the aluminum inside is oxidized to alumina first because of the low Gibbs free energy. In addition, the aluminum enrichment phase shows a network structure and surrounds a copper-rich phase. However, the total amount of dense alumina phase is small but evenly distributed between the boundaries of copper-rich regions, protecting the copper phase and greatly reducing the oxidation of capsules. When the self-sealing reaction at the inlet and core-shell boundary is complete, the capsule is sealed. The path of oxygen into the capsule disappeared, and the oxygen concentration inside the capsule begins to decrease gradually as the reaction progresses. Reaction 3 dominates the final oxidation reaction in the core, and \( \Delta G^0 \), Gibbs free energy of reaction 3, was calculated as \(-104.5 \text{ kJ/mol} \) at 1100 °C. According to the Gibbs free energy, eq 4, the equilibrium constant \( K_p \) of reaction 3 was calculated as \( 9.16 \times 10^4 \) when the temperature was up to 1100 °C. Therefore, the equilibrium partial pressure of oxygen \( P_{O_2} \) was estimated to be 0.06 Pa using eq 5. When the partial pressure of oxygen in the oxide layer is lower than 0.06 Pa, all of the reactions in the capsule stop completely.

\[
2\text{Al}_2\text{O}_3 + 2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuAl}_2\text{O}_4 \quad (3)
\]

\[
\Delta G^0 = -RT \ln K_p \quad (4)
\]

\[
K_p = \frac{[a_{\text{CuAl}_2\text{O}_4}]^2}{[a_{\text{Al}_2\text{O}_3}]^2[a_{\text{Cu}}][P_{O_2}]} \quad (5)
\]

In conclusion, an extremely low weight increase ratio proves that the in situ seal has good airtightness and prevents oxygen from entering the capsule, which is in good agreement with our hypothesis. Adding a small amount of aluminum powder to the copper bead gap successfully forms a network structure of alumina in the core material. This further reduces the oxidation rate of copper in the core metal. Thus, this EPCM shows good oxidation resistance and durability for long-term operation in air.

3.3.2. Heat-Transfer Rate. In order to further verify the durability after a long exposure test, a Cu−8.40% Al EPCM...
sample was prepared and exposed to ambient air at 1200 °C for 200 h. Figure 16 summarizes the center temperature behavior of the samples under a constant temperature heating of 500 °C to compare the heat-transfer performance before and after exposure.

According to the center temperature chart, the Cu−8.40% Al EPCM showed a faster heat-transfer rate and superior heat-transfer performance at 500 °C compared to conventional solid alumina spheres of the same size. The maximum temperature difference between the EPCM and the alumina solid ball was measured over 100 K due to the dense inner structure and high thermal conductivity of the Cu−8.40% Al alloy. Compared with the Cu−8.40% Al EPCM sample after 2 h exposure, there was no significant difference in the center temperature curve after 200 h of exposure in terms of heat-transfer performance. This result indicates that the phase and structure of the PCM did not change significantly after long-term exposure to high-temperature air. As a composite heat storage body, the Cu−8.40% Al EPCM showed chemical stability during long-term recycling.

3.3.3. Mechanical Strength Test. Figure 17 shows the damage load used to evaluate the mechanical strength after long-term exposure. After being heated at 1200 °C for 2 h and cooled to room temperature, the Cu−8.40% Al EPCM showed a damage load of 3.7 kN measured from the top seal. It is considered that the stress concentration is reduced because the inside of the shell is filled with the core and the gap between the core shells is small. In addition, it can be seen that the stress–displacement relationship is not a linear and brittle fracture peculiar to ceramics but a zigzag shape in which stress is released. It is presumed that this is because there is a partial joint between the core shells, which complicates the progress of fracture. By observing the broken fragments, it was found that the cracks extended from the joint of the seal to the shell inlet. Thus, it can be inferred that the inlet of different combinations is the part that is most likely to generate a stress concentration. After long-term exposure to high temperatures in the air, the phase in the seal exhibited slight changes because of slow oxidation reactions, and the load curve gradually becomes smooth from jagged and more similar to the brittle fracture of ceramics. It is not clear that this phenomenon is due to the reaction or the variation in ceramics. The Cu−8.40% Al EPCM maintained good mechanical strength after the 200 h exposure test. Reducing the loss of mechanical strength after long-term utilization will be an important objective in future research. The data obtained in this study can be used as a reference for the design of packed beds in the future.

4. CONCLUSIONS

A series of experiments were conducted to determine the in situ sealing mechanism and durability of Cu−(5−10%) Al EPCM to develop a Cu-based PCM for high temperatures. The major conclusions are as follows:

1. A Cu-based EPCM with a simple fabrication process was proposed, where the Cu beads plus the Cu−Al alloy [Cu−5−10%(average) Al] is the core, and the integrated shell is formed by black alumina.

2. When compared with the pure Cu EPCM, the Cu−(5−10%) Al EPCM effectively reduced the reactivity between CuO and the alumina shell by filling the Cu−Al atomized powder into the space of copper beads. The developed Cu-based EPCM exhibited characteristics such as high packing ratio, dense interior structure, and in situ sealing. Al and Cu distributed uniformly at the inlet were oxidized to alumina and CuO, respectively, at 1200 °C in air and subsequently formed CuAl2O4. The CuAl2O4 layer was generated at the inlet and boundary, and the capsule was in situ sealed, which prevented oxygen from diffusing into the capsule. Because of in situ sealing, no leakage was found in the EPCM after heating, and there was no trace of strong reactions between the inner core and shell. The self-sealing nature simplifies the production process of the EPCM, which is beneficial for mass production.

3. In the core material, aluminum powder is preferentially oxidized to alumina forming a network structure. The alloy in copper-rich areas is protected from oxidation and shows relative stability in thermal properties and distribution during subsequent cycles.

4. The outstanding durability of the EPCM was confirmed by oxidation ratio measurements, heat-transfer rate tests, and damage load experiments. After 400 h of air...
exposure test at 1100 °C, the weight of the Cu–Al EPCM increased by only 3.5%, which confirmed the excellent oxidation resistance of the Cu beads plus the Cu–Al alloy [Cu–5–10%(average) Al] EPCM. In addition, there was no significant heat-transfer performance change before and after exposure, which indicates that the product could maintain relatively stable physical properties and internal structure after long-term utilization.

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Notes
The authors declare no competing financial interest.

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