多孔体担持型化学蓄熱材の性能評価

PERFORMANCE ASSESSMENT OF THE POROUS SOLID SUPPORTED CHEMICAL HEAT STORAGE MATERIAL

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Abstract The solid metal compound is usually used as the heat storage material for the chemical heat pump that used the medium and low temperature heat source. The solid base metal compound functions as a heat storage material of chemical heat pump by assuming water to be a working medium. The problems is the heat storage material's reactive deterioration due to the repetition heat storage and heat release, another problem is the difficulty of the rational design of the heat regenerator by heat storage material's alteration in volume. In the present study, "the porous solid supported chemical heat storage material's creation" was proposed. The solid base metal compound of the medium and low temperature heat storage material was supported into the porous solid, the repeated durability and the morphological stability was examined. As a result, the porous solid supported chemical heat storage material for chemical heat pumps because it maintained the reactivity and ensured the morphological stability.

1. INTRODUCTION

The unused medium and low temperature waste heat is exhausted in the industrial activity. The advanced technology used development of the medium and low temperature waste heat of about 100-400°C is needed from viewpoint of the energy resource and the environment. An efficient heat storage function is needed for recovery of medium and low temperature waste heat. The chemical heat pump uses the chemical reaction which a high heat storage density and the long-term high storage. The solid metal compound is usually used as the heat storage material for the chemical heat pump that used the medium and low temperature heat source. The solid base metal compound (magnesium oxide, calcium oxide, calcium sulphate) functions as a heat storage material of the chemical heat pump by assuming water to be a working medium [1], [2]. The development research is progressed centering on the improvement of the heat exchanger type heat storage machine for making of the use heat storage material that is reaction promotion.

Though, there is no method for solving the following two problems, and the development research stagnates a little in recent years due to the difficulty. One of the problems is the heat storage material's reactive deterioration due to the repetition heat storage and heat release, another problem is the

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difficulty of the rational design of the heat regenerator by heat storage material's alteration in volume is enumerated.

In the present study, "the porous solid supported chemical heat storage material's creation" was proposed. The solid base metal compound of the medium and low temperature heat storage material was supported into the porous solid, the repeated durability and the morphological stability was examined.

2. POROUS SOLID SUPPORTED CHEMICAL HEAT STORAGE MATERIAL

2.1 Development of porous solid supported chemical heat storage material

The carbonaceous porous body was used as a material of the porous body. The porous solid supported chemical heat storage material uses a new method of the heat storage material into carbonaceous porous body.

It shows development process in Figure 1. First, it is mixed with PVA(polyvinyl alcohol),heat storage material (calcium nitrate) and starch. Secondly, after polyvinyl Formal resin by crossed link, starch is removed. Finally, it becomes the porous solid supported CaO of chemical heat storage material by heat treating at 850°C under an inert atmosphere.

The SEM image and the EDX image of the sample made by using this method are shown in Figure 2. This porous solid supported chemical heat storage material made break up and granulating the mean particle size was 1mm following performance assessment experiment. CaO was supported the carbonaceous matrix of fine porous of $5-10\mu$ m in the SEM image corresponding EDX image. The supported rate of the development sample was 74wt% as high as a standard CaO.



Figure 1 Process model of carbonaseous porous solid supported heat storage material



- Figure 2 SEM of preproduction carbonaseous porous solid supported heat storage material
 - (a) SEM photograph of carbonaseous porous solid supported heat storage material
 - (b) EDX photograph of calcium component
 - (c) EDX photograph of carbon component

2.2 Experimental arrangement and method of performance assessment

The following experimental assessments were done about the sample made for trial purposes.

The highest rising temperature according to an increase in the repeat count for the raw chemical heat storage material and the porous solid supported chemical heat storage material was assessed. It was compared the reaction degradation on the raw chemical heat storage material and the porous solid supported chemical heat storage material by the assessment of depression of repeat count with a highest rising temperature.

It was checked the sample of the form maintenance by SEM observation and it was checked to inhibit the agglomeration in the fine pores on the porous solid supported chemical material.

It shows the closed system experimental arrangement for the simulated chemical heat pump in Figure 3(a).



Figure 3 Experimental arrangement(a) and derails of reactor(b)

This experimental arrangement is configured for the reactor and the evaporative condenser using graduated cylinder with the controlled in an electric furnace and the temperature of evaporative condenser is controlled using the water tank type constant temperature bath. Also the experimental arrangement was degassed in order to be closed system the vacuum oil pump and was verified the pressure change by the pressure meter fit in the pipe arrangement. The sample was filled up from the reactor bottom to 12mm high as showed in Figure 3(b). The thermocouple was inserted in the central portion of radial direction of inside of a sample and the bottom of reactor outside. The temperature of inside of a sample was used for temperature assessment on. In case of raw Ca(OH)₂ sample weight was 15g and in case of the porous solid supported Ca(OH)₂ was 14g(weight of Ca(OH)₂ was 11g). This is proved as same condition to the packing volume.

It shows following experiment condition of heat release. First, the sample is filled the reactor, it degases with the vacuum pump and it makes it to the water vapor. The temperature of the reactor is adjusted to 60°C and the temperature of the condenser is set to 60°C. Next, water vapor moves to the reactor by opening the valve. The temperature change when water reacted with calcium oxide was measured.

3. RESULT OF EXPERIMENT AND CONSIDERATION

It is that one example of the temperature change of heat release for the raw heat storage material and the carbonaceous porous solid supported heat storage material is shown in Figure 4, Figure 5. The raw heat storage material and the porous solid supported heat storage material descended to an initial temperature it had risen up to the highest attainment



Figure 4 Changes of temperature rize(Δ T) accompanied with repeat of release for raw Ca(OH)₂



Figure 5 Changes of temperature rize(Δ T) accompanied with repeat of release for carbonaseous porous solid supported Ca(OH)₂

temperature. For the raw heat storage material, the temperature rose up to 307°C by the second heat release but the temperature rose by the sixth heat release only at 107°C. On the other hand, the temperature rose up to 261°C by the second heat release and the temperature rose up to 278°C by the 15th heat release for the porous solid supported heat storage material, because the reduction in temperature of the porous solid supported heat storage material was less than that of the raw heat storage material. The relation between a repeat count and rising temperature for the raw heat storage material and the porous solid supported heat storage material is shown in Figure 6. From Figure 6, the rising temperature of the heat storage material at the first and second times are higher than the porous solid supported storage material, while the temperature of the raw heat storage material decreases rapidly since third times in contradistinction to rising temperature is maintained though the repeat count of the porous solid supported storage material increases. As the result, the porous solid supported heat storage material is considered to control the deterioration of reactivity for the repeat test.

Next, the before and after SEM image of repeat for the raw heat storage material and the porous solid supported material are shown in Figure 7. The particle size of the raw heat storage material was large by the agglomeration in repeat after. Compared, the particle size of the porous solid supported storage material wasn't increased in repeat before and after. The porous solid supported heat storage material was considered the agglomeration by this result.

4 CONCLUSION

The proposed porous solid supported heat storage material was developed and was assessed the highest rising temperature and the shape observation of solid in the repeat count. As a result, the following conclusions were obtained within the range of the practical experiment.

In the carbonaceous porous solid supported $Ca(OH)_2$, the agglomeration of the particle was controlled through the repeat count increased. It was verified that the highest rising temperature of the carbonaceous porous solid supported $Ca(OH)_2$ was maintained in the heat release process and $Ca(OH)_2$ was supported in an empty hole of the carbon and its shape was maintained.

Consequently the carbonaceous porous solid supported $Ca(OH)_2$ maintained the reactivity and ensured the morphological stability. That is, it is thought the porous solid supported chemical heat storage material functions as a heat storage material for chemical heat pumps.

5 **REFERENCES**

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Figure 6 The highest rising temperature accompanied with repeat count



Repeat before Repeat after Figure 7 SEM image of heat storage material-raw Ca(OH)2





Repeat before

Repeat after

Figure 8 SEM image of heat storage material- carbonaceous porous solid supported Ca(OH)2