Measurement of Thermophysical Properties of Thermal Storage System
- Effect of Heat Transfer Media -

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SUMMARY

In order to improve the low heat transfer rate in $CaCl_2 \cdot nNH_3$ system as one of thermal storage systems, the heat transfer media was mixed with $CaCl_2 \cdot 8NH_3$ system and measure thermophysical properties, the effective thermal conductivity (λ) and the effective thermal diffusivity (α) of $CaCl_2 \cdot 8NH_3$ + heat transfer media system were measured by the arbitrary heating method and compared with those of $CaCl_2 \cdot 8NH_3$ system. The value of λ of $CaCl_2 \cdot 8NH_3$ + heat transfer media system was approximately 2～3 times larger than that of $CaCl_2 \cdot 8NH_3$ system, and the value of α of $CaCl_2 \cdot 8NH_3$ + heat transfer media system was approximately 2 times larger than that of $CaCl_2 \cdot 8NH_3$ system. It is seemed that λ and α of $CaCl_2 \cdot 8NH_3$ + heat transfer media system are influenced by the packed density of this system.

KEY WORDS: thermal storage system, thermophysical properties, ammine complex, calcium chloride, ammonia, arbitrary heating method, heat transfer media

1. INTRODUCTION

Recently, the possibility of significant global warming resulting from emissions of greenhouse gases by fossil fuel combustion has become an important concern within the international community. For thermal energy storage systems utilizing low heat sources as a solar energy or a hot effluent (approximately 353～373 K), the processes using the chemical reaction of anhydrous salt with ammonia (NH_3) have been proposed and discussed for its practicably[1～6]. For example, some prototypes of energy storage unit using $CaCl_2 \cdot nNH_3$ system have been designed and measured these performances [3～6].

The reaction products from anhydrous salts and ammonia are referred to as ammoniated salts or ammine complexes and the state is either solid or liquid. In this study, the chemical reaction of $CaCl_2 \cdot 4NH_3$ with $4NH_3$[5,6,8,9] was chosen here for the thermal energy storage system. In this reaction, ΔH (enthalpy change) is 43.8 kJ/mol-NH_3 [1], the value of which is higher than the latent heat of vaporization of liquid NH_3, 23.4 kJ/mol-NH_3 [2]. However, this chemical reaction system has a low transfer rate through the solid phase where powdered crystal is packed with NH_3 gas, and this reaction rate is controlled by the heat transfer rate. In the author's previous work [8,9], in order to measure the thermophysical properties (effective thermal conductivity and effective thermal diffusivity) of $CaCl_2 \cdot nNH_3$ system, the measurement unit has been developed by the arbitrary heating method using Laplace transform and measured the effective thermal conductivity (λ) and the effective thermal diffusivity (α) of $CaCl_2 \cdot nNH_3$ system.

In this study, in order to improve the low heat transfer of this solid-gas reaction system, the titanium sponge (Ti) as the heat transfer medium was inserted in this reaction system, and λ and α as the thermophysical properties of $CaCl_2 \cdot 8NH_3$ + Ti system were measured and compared with those of $CaCl_2 \cdot 8NH_3$ system.

2. PRINCIPLE OF MEASUREMENT

2.1. Principle of measurement and measurement system

In this study, this principle of measurement is only shown. Regarding the principle of this measurement method in detail, refer to the arbitrary heating method by Iida *et al.*[7] and the author's previous work [8,9]. Figure 1 shows the principle of measurement.

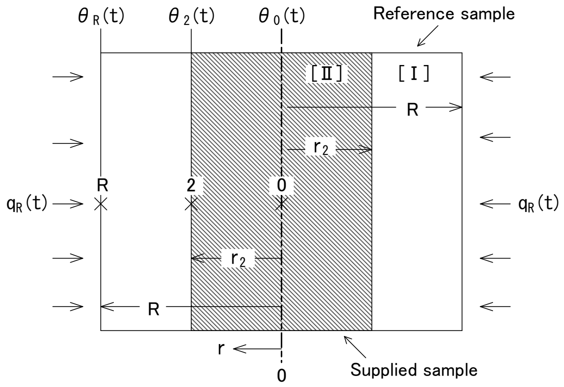


Figure 1. Principle of measurement

Considering the infinite tubular sample [I] around the infinite cylindrical sample [II] in Figure 1. In this experiment, the supplied sample is the case of cylindrical sample [II] . Hence tubular sample [I] is the case of reference sample. Assuming the heat flux is only direction of radius and the contact resistance is negligible, and the symbol × is expressed a measuring point of temperature and the measuring point 2 is defined as the boundary surface. The temperature response $\theta(r_i, t)$ at each measuring point *i* ($i = 0, 2$,R) is rewritten as $\theta_i(t)$, Laplace integration of each point is expressed by

$$\overline{\theta}_i = \int_0^\infty e^{-st}\theta_i(t)dt \tag{1}$$

In this measurement system, the temperature responses of central point in the cylindrical sample as the supplied sample and surface point of the reference sample were measured at the same time in Figure 1. On the other hand, heat flux $q(r,t)$ is given by Fourier's equation and transformed by Laplace transform, and then given by

$$\overline{q} = -\lambda\sqrt{\frac{s}{\alpha}}\left\{CI_1(\sqrt{s/\alpha}\cdot r) + DK_1(\sqrt{s/\alpha}\cdot r)\right\} \tag{2}$$

Assuming α_{I}, λ_{I} and $c_{p\,\mathrm{I}} \times \rho_{\mathrm{I}}$ （c_p : specific heat, ρ : density） are thermal diffusivity, thermal conductivity and heat capacity of the reference sample, respectively, and are well known. In ［II］, $q(0,t) = 0$. Hence $(\overline{q})_{r=0} = 0$. Thus $D_{\mathrm{II}} = 0$ in equation (2), and substitution of $I_0(0) = 1$ into equation (2), then given by

$$\overline{\theta}_0 I_0(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2) - \overline{\theta}_2 = 0 \tag{3}$$

where α_{II} is thermal diffusivity of the supplied sample.

Hence, in this case, $\overline{\theta}_2 / \overline{\theta}_0$ can be calculated. Thermal diffusivity α_{II} is calculated from the relation between $\overline{\theta}_2 / \overline{\theta}_0$ and $\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2$ 7,8,9).

Then thermal conductivity of the supplied sample λ_{II} is given by the following equation.

$$\frac{\lambda_{\mathrm{II}}}{\lambda_{\mathrm{I}}} = \sqrt{\frac{\alpha_{\mathrm{II}}}{\alpha_{\mathrm{I}}}} \frac{1}{I_1(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2)} \frac{1}{\overline{\theta}_0} \left\{ C_{\mathrm{I}} I_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - D_{\mathrm{I}} K_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) \right\} \tag{4}$$

Then C_{I} and D_{I} are given by

$$C_{\mathrm{I}} = \frac{\overline{\theta}_2 K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - \overline{\theta}_R K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)} \tag{5}$$

$$D_{\mathrm{I}} = \frac{\overline{\theta}_2 I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - \overline{\theta}_R I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R)} \tag{6}$$

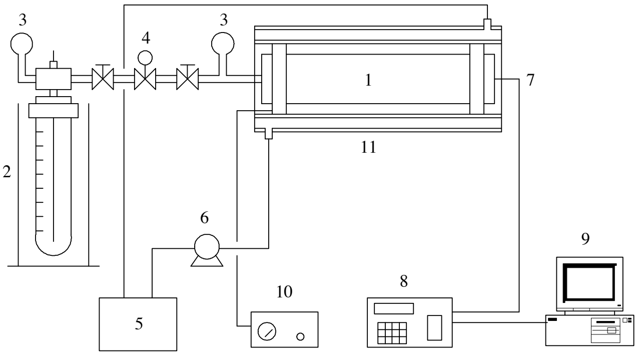
where I_0 and K_0 are modified Bessel functions of the first and the second kind of zero-order, respectively.

3. EXPERIMENTAL SECTION

3.1 Experimental apparatus

Figure 2 schematically shows the experimental apparatus of the measurement system. This system consists of measurement unit (cell) as the reactor, NH_3 glass vessel, pressure regulator valve, pressure gauges, thermocouples and constant temperature water bath. The measurement cell is made of stainless steel and it is covered with water jacket, which can control the temperature in the measurement cell. The NH_3 vessel is pressure resistance glass vessel, and the volume of the liquid NH_3 is measured by a microscope. In order to insulate the measurement unit from the surroundings, the apparatus is wrapped foamed polystyrol. The temperature in this unit is measured by using C-A type thermocouples with the digital thermometer, and the temperature responses as the digital signals are transferred to the micro computer and analyzed.

The amount of liquid NH_3 transferred to the measurement cell from the NH_3 vessel can be measured by the microscope. The temperature of the measurement cell, unit and the NH_3 vessel are controlled by using constant temperature bath having minimum accuracy within ± 0.1 K separately. The pressure in each vessel is measured by Bourdon gauge. The pressure control in the measurement cell is carried out using the pressure regulator valve.



1 : Measurement cell, 2 : Pyrex glass vessel,
3 : Pressure gauge, 4 : Pressure regulator valve,
5 : Constant temperature bath, 6 : Pump,
7 : Thermocouple, 8 : Digital thermometer,
9 : Micro Computer, 10: Temperature controller,
11: Water jacket

Figure 2. Schematic diagram of measurement unit

This measurement cell consists of two major units, a stainless steel pipe and a reinforced pressure proof glass tube as the reference sample (Pyrex 7740: OD: 40.0 mm, ID: 32.0 mm) , and the temperature responses are measured by the stainless steel covered C-A thermocouples, which are inserted in the measurement cell. Regarding the measurement cell in detail, refer to the author's previous work[8)].

3.2 Experimental Procedure

3.2.1. Preparing for $CaCl_2 \cdot 8NH_3$ system (Ammoniation)

$CaCl_2$ of 0.218 mole (approximately 24.2 g) was crushed and was dried at 773 K for 5 hours by an oven. The dried $CaCl_2$ powder sample mixed with Ti (approximately 72.6 g) was placed in the measurement cell, and it was sealed, and worked by the vacuum pump in order to remove air and any water from this measurement cell.

After liquid NH_3 was charged in the NH_3 vessel, its volume was measured by the microscope rapidly and recorded. Then this measurement cell was connected with the NH_3 vessel shown in Figure 2. NH_3 gas moved to the measurement cell through the pressure regulator valve keeping constant pressure (0.5 MPa) during the reaction, and mole number of NH_3 absorbed to pure $CaCl_2$ was calculated from this liquid NH_3 volume change in the NH_3 vessel. When 8 moles of NH_3 was absorbed to the pure $CaCl_2$, the experiment of ammoniation was just finished.

3.2.2 Measurement of thermophysical properties

After temperature of cell was settled with the measurement temperature and the temperatures of measuring points were stabilized, and start heating of the measurement cell by charging electricity to Ni-Cr wire, where heating rate and maximum heating temperature are 5 K/min. and 10 K, respectively, in order to avoid the violent reaction in the measurement cell during the measuring time. Temperature responses of the thermocouples were measured by the digital thermometer and were recorded to the micro computer system, and the scan rate is every 9 seconds and the measurement time is 30 minutes.

4. RESULTS AND DISCUSSION

Figure 3 shows the relation between λ of $CaCl_2 \cdot 8NH_3$ + Ti system and temperature (with λ of $CaCl_2 \cdot 8NH_3$ system). The value of λ of $CaCl_2 \cdot 8NH_3$ + Ti system was approximately 0.3～0.9 W/(m・K) in the measuring temperature range

(290 to 350 K). The value of λ of this system increased with the increase in temperature in the measuring temperature range. The value of λ of this system was approximately 2～3 times larger than that (0.1～0.5 W/(m·K)) of $CaCl_2 \cdot 8NH_3$ system[9].

Figure 4 shows the relation between α of $CaCl_2 \cdot 8NH_3$ + Ti system and temperature (with α of $CaCl_2 \cdot 8NH_3$ system). The value of α of $CaCl_2 \cdot 8NH_3$ + Ti system was approximately 0.10～0.35 ($\times 10^{-6}$ m^2/s) in the measuring temperature range (290 to 350 K). The value of α of this system increased with the increase in temperature in the measuring temperature range. The value of α of this system was approximately 2 times larger than that (0.04～0.17 ($\times 10^{-6}$ m^2/s)) of $CaCl_2 \cdot 8NH_3$ system[9]. It is seemed that this tendency is similar to that of λ in this system.

Regarding the effect of the mixing Ti as the heat transfer media, it is found the heat transfer rate on both results of λ and α are improved in this system, and it is seemed that λ and α of $CaCl_2 \cdot 8NH_3$ + Ti system are influenced by the packed density (ρ_{bulk}: $CaCl_2 \cdot 8NH_3$ + Ti system: 0.75 x 10^3 kg/m^3, $CaCl_2 \cdot 8NH_3$ system: 0.32 x 10^3 kg/m^3) of this system.

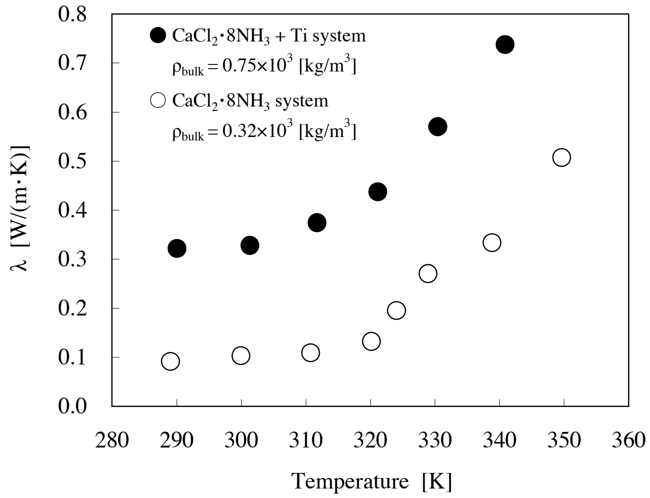


Figure 3. Relation between λ of $CaCl_2 \cdot 8NH_3$ + Ti system and temperature

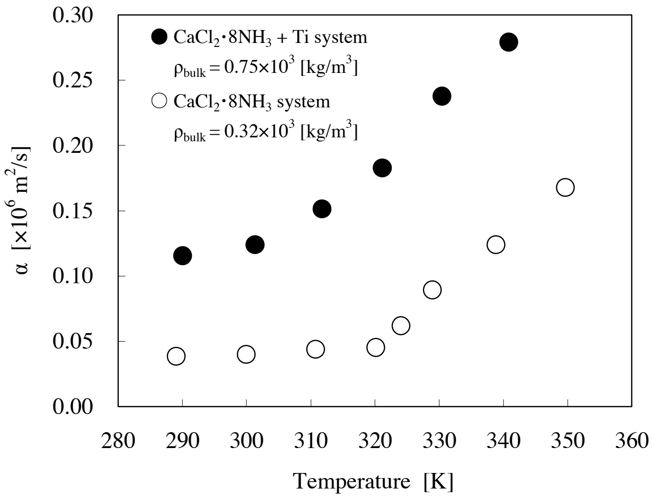


Figure 4. Relation between α of $CaCl_2 \cdot 8NH_3$ + Ti system and temperature

In general, it is well known thermal conductivities of solids depend on many factors and are difficult to measure or predict. In particular, in porous solids, for example, the thermal conductivity is strongly dependent on the void fraction (related to the packed density (ρ_{bulk}) in this experiment), the pore size and the fluid contained in the pore[10]. It is necessary to investigate the detailed effect of the void fraction and /or the packed density for the effective thermal conductivity of this system.

5. CONCLUSIONS

In this study, in order to develop the thermal energy storage system using $CaCl_2 \cdot nNH_3$ system and improve the low heat transfer rate in this reaction system, Ti as the heat transfer media (mixed with 3 times of $CaCl_2$ by weight) was mixed with $CaCl_2 \cdot 8NH_3$ system, and the effective thermal conductivity λ and the effective thermal diffusivity α as thermophysical properties of $CaCl_2 \cdot 8NH_3$ + Ti system were measured by the arbitrary heating method using Laplace transform and compared with those of $CaCl_2 \cdot 8NH_3$ system. As the results of the effect of the mixing of Ti, the value of λ (0.3～0.9 W/(m・K) of $CaCl_2 \cdot 8NH_3$ + Ti system was approximately 2～3 times larger than that (0.1～0.5 W/(m・K)) of $CaCl_2 \cdot 8NH_3$ system, and the value of α (0.10～0.35 ($x10^{-6}$ m^2/s) of $CaCl_2 \cdot 8NH_3$ + Ti system was approximately 2 times larger than that (0.04～0.17 ($x10^{-6}$ m^2/s)) of $CaCl_2 \cdot 8NH_3$ system. It is seemed that λ and α of $CaCl_2 \cdot 8NH_3$ + Ti system are influenced by the packed density (ρ_{bulk}: $CaCl_2 \cdot 8NH_3$ + Ti system: 0.75 x 10^3 kg/m^3, $CaCl_2 \cdot 8NH_3$ system: 0.32 x 10^3 kg/m^3) of this system.

ACKNOWLEDGEMENTS

The author is grateful to Professor Hideki Yamamoto of Kansai University for the support to this study.

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