ABSTRACT

The melting behavior of CaCl$_2$·$n$H$_2$O ($n=6.00, 7.35$) coexisting with the inorganic powders was investigated with DSC measurement. For $\alpha$-Al$_2$O$_3$ powder/ CaCl$_2$·6.00H$_2$O coexisting system, the melting point of the hydrate was lowered and the molar enthalpy of melting decreased both with the decreases of the liquid content and with the increase of the specific surface area of the powder. The observed melting point correlated to the transition point obtained by the electrical conductivity. For $\alpha$-SiC powder/ CaCl$_2$·6.00H$_2$O coexisting system, the melting point and the molar enthalpy of fusion for hydrate were constant in the range of 17.2-48.0 vol% of the hydrate content. These behaviors led that the phase transition of hydrate near the surface of the solid phase was significantly influenced by the hydrophilicity of solid phase surface.

Experimental

The solid phase used in this study were high-purity $\alpha$-Al$_2$O$_3$ powder and high-purity $\alpha$-SiC powder which had various surface areas. The physical aspects of them are shown in Table 1. The methods of the pretreatment and characterization of powders have been reported(6). CaCl$_2$ hydrates were prepared from CaCl$_2$·2H$_2$O (supplied Nakalai Tesque
Table I. Physical aspects of powders.

| Species | Sample no. | Specific surface area [m²/g] | Particle size [µm] | Grade            |
|---------|------------|------------------------------|-------------------|------------------|
| α-Al₂O₃ | 2          | 0.6                          | 75                | Showa calcined   |
|         | 5          | 3.0                          | 0.7               | Showa low soda   |
|         | 7          | 5.0                          | 0.4               | Showa ultra pure |
|         | 9          | 25.3                         | 0.6               | Showa ultra pure |
| α-SiC   | S          | 1.1                          | <19               | Kishida (#800)   |

For DSC measurement, α-Al₂O₃ powder was mixed thoroughly with the hydrate by using an agate mortar and immediately sealed in an aluminum pan. The volume fractions of the liquid phase were ranged in 17.2-48.0 v/o. The measurement was carried out for the frozen sample on heating from -80 to 60°C with DSC/20 thermal calorimeter (Seiko Instruments & Electronics Ltd.).

The Scanning speed was 5°C/min. The temperature calibration was carried out by using the melting points of 1,2-dichloroethylene (m.p.: -35.3°C) and diphenylether (m.p.: 30°C). The area of the endothermic peak on DSC curves, attributed to melting of CaCl₂·6H₂O, was calculated with the Kambe’s method (6). The volume fraction was calculated by the same method as described previously (7).

The obtained DSC curve included the heat capacity of the powder and hydrate with the latent heat of fusion as a base line. It was corrected to determine the heat of fusion for the hydrate by subtracting the base line. In order to discuss the influence of the solid phase on the melting behavior of the hydrate, the DSC curves were represented as the heat balance for the liquid phase per unit area of the solid phase, \( \frac{\Delta Q}{\Delta T} \), which was calculated as follows;

\[
\frac{\Delta Q}{\Delta T} = \frac{\Delta Q}{\Delta T} \div (S_w \cdot W)
\]

where \( \frac{\Delta Q}{\Delta T} \), \( S_w \) and \( W \) are the heat balance of the sample, the specific surface area and the weight of the powder, respectively.

Because the hydrate is lied on the solid surface with having a certain thickness as mentioned in Ref. 5., the apparent average thickness of the liquid phase layer, \( d \), was defined as following;

\[
d = \frac{V_{\text{liq}}}{(S_w \cdot W)}
\]

where \( V_{\text{liq}} \) is the total volume of the liquid phase.

Then the molar enthalpy of melting, \( \Delta H_m \), was calculated as follows,

\[
\Delta H_m = -M \int_{T_1}^{T_2} \frac{\Delta Q}{\Delta T} dT \div d \cdot \rho
\]
where $M$ is the molecular weight of CaCl$_2·6$H$_2$O (219.1), $\rho$ is density of the hydrate melt above the melting point, and $T_h$ and $T_l$ are temperatures of the higher end and the lower end of the peak, respectively. The calculated value is regarded to the heat of fusion for the hydrates.

**Results and Discussion**

The DSC curves for various kinds of $\alpha$-Al$_2$O$_3$ powders/ CaCl$_2·6$H$_2$O coexisting systems are shown on Figure 1. For each sample, the endothermic peak assigned to melting was observed. The peak shifted toward the lower temperature with the decrease of the liquid content.

![DSC curves for $\alpha$-Al$_2$O$_3$ powder/ CaCl$_2·6$H$_2$O coexisting system.](image)

**Fig.1.** DSC curves for $\alpha$-Al$_2$O$_3$ powder/ CaCl$_2·6$H$_2$O coexisting system. $\alpha$-Al$_2$O$_3$ powder in (a): no.5 and in (b): no.9.
For the system which contains $\alpha$-$\text{Al}_2\text{O}_3 \ (\text{no. 5})$ powder (Fig. 1(a)), the variation of the endothermic peak area was not linearly proportional to the content of the liquid phase. Especially, for 25.5 v/o of the liquid phase, the endothermic peak was very small. Also, the DSC curves at the lower end of the peak were overlapped for each samples. In order to discuss on the melting behavior, the models of the liquid layer near the solid surface were presented at Figure 2. It is suggested that the melting of the hydrate starts from the vicinal region on the powder surface at a lower temperature than the ordinary melting point. The smaller peak than that expected for the system containing little hydrate, which is in a state of the thin layer on the powder surface, led to the decrease of the molar enthalpy of melting for the hydrate near the powder. In contrast, the peak area was remarkably large for the system with the higher hydrate content. It is suggested that the molar enthalpy change for melting was close to that of the bulk state at the distant region from the solid surface. Thus, the molar enthalpy change for melting of the hydrate was correlated with the distance from the solid surface. The DSC curves for the system containing $\alpha$-$\text{Al}_2\text{O}_3 \ (\text{no. 9})$ powder are shown in Figure 1(b). It shows that the diminution of the peak area is promoted with the increase of the specific surface area of the $\alpha$-$\text{Al}_2\text{O}_3$ powder. These results suggested that the phase transition of the hydrate near the powder surface was influenced by the existence of the solid phase.

The relationship between the total enthalpy of the melting, $\Delta H_{\text{m}}^{\text{total}}$, with a normalized

![Figure 2. Models for the vicinal layer.](image-url)
Specific surface area: 0.6 m$^2$/g

[CaCl$_2$·6H$_2$O] (mmol/m$^2$ (α-Al$_2$O$_3$))

Fig. 3. (a) Relationships between $\Delta H_m^{\text{total}}$ and the content of the hydrate for α-Al$_2$O$_3$ (no. 2) powder/ CaCl$_2$·6.00H$_2$O coexisting systems. (b) Variations of $\Delta H_m$ with the liquid content for various kinds of α-Al$_2$O$_3$ powders/ CaCl$_2$·6.00H$_2$O coexisting systems.

surface area, per 1.0 m$^2$, of the powder and the content of the hydrate for α-Al$_2$O$_3$ (no. 2) powder/ CaCl$_2$·6H$_2$O coexisting systems was shown in Figure 3(a). The $\Delta H_m^{\text{total}}$ increased with the amount of the hydrate phase, but is not proportional with the amount of the hydrate. It is suggested that the liquid phase near the solid surface differs from that in the bulk region. The molar enthalpies for the melting of the hydrate, $\Delta H_m$, in the various kinds of α-Al$_2$O$_3$ powder/ CaCl$_2$·6H$_2$O coexisting systems was shown in Figure 3(b). It is shown that $\Delta H_m$ increased with the hydrate content and was levelled off in the composition range above ca. 40 v/o of the liquid phase. $\Delta H_m$ also decreased with the increase of the surface area of α-Al$_2$O$_3$. If it can be assumed that the molar enthalpy change for melting of CaCl$_2$·6H$_2$O is constant, these results suggest that the hydrate melt partially solidifies in the vicinity of the surface of α-Al$_2$O$_3$ powders.

On the basis these results, the existence of the non-frozen liquid phase, $\phi_{NFL}$, can be defined thermodynamically as follows,

$$ \phi_{NFL} = 1 - \frac{\Delta H_{SL}}{\Delta H_{bulk}} $$

where, $\Delta H_{SL}$ and $\Delta H_{bulk}$ were the molar enthalpies of melting of the hydrate for the solid/liquid coexisting system and the bulk system, respectively. Thus, variations of $\phi_{NFL}$ with the hydrate content for α-Al$_2$O$_3$ (no. 2 and no. 9) powders/ CaCl$_2$·6.00H$_2$O coexisting system

Fig. 4. Variations of $\phi_{NFL}$ with the liquid content for α-Al$_2$O$_3$ powders/ CaCl$_2$·6.00H$_2$O coexisting systems.
are shown in Figure 4. The decrease of the hydrate content led to the relative increase of the region of the non-frozen liquid phase. It indicates that the freezing of the hydrate was hindered by the solid surface. In the solid/liquid coexisting system, it is known generally that the solid particle acts as a seed for crystalline nucleation. However, in this case, the melt was stabilized by too many solid particles.

The non-frozen liquid contributes to form the electric conduction path at a temperature even below the melting point, whereas the solidified crystalline hydrate behaves as the electric insulator. According to the results of the electric conductivity (5), the deflection of the conductivity was observed at the melting point on the plots of $\ln \sigma$ vs. $1/T$ during heating. However, during cooling, the solidification did not occur and the deflection point was not observed. So, the electrical conductivity measured in the cooling process were that of the supercooled hydrate. The ratio of the electrical conductivities on cooling to that on heating, $\sigma_{\text{cool}}/\sigma_{\text{melt}}$, at the various temperatures indicates the extent of the decrease of paths owing to the solidification of the hydrate.

The molar entropy of melting means the structural change of the hydrate for the phase transition. Generally, the molar entropy of melting, $\Delta S_m$, can be calculated by the following equation for the crystalline solid,

$$T_m = \frac{\Delta H_m}{\Delta S_m} \quad [5]$$

where, $T_m$ was the melting point of the crystalline solid. However, in this system, the peak profile was broadened and the melting point varied with the liquid content. Thus, the value of $\Delta S_m$ cannot be simply calculated. In this case, $\Delta S_m$ was calculated by the same manner as that for the $\Delta H_m$ by using Eq. [6].

$$\Delta S_m = -\int \left( \frac{\Delta Q/\Delta T}{T} \right) dT \quad [6]$$

As shown in Eq.[6], if the melting proceeds only at a certain temperature, $T_m$, Eq.[5] was applied. The variations of $\Delta S_m$, with the hydrate content for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders/ $\text{CaCl}_2\cdot6.00\text{H}_2\text{O}$ coexisting systems are shown in Figure 5. These results showed that the phase transition did not fully occur and the liquid phase was prevented to change its structure. Comparing with Figure 3(b), the same tendency was observed as $\Delta H_m$. Also, the decrease of $\Delta S_m$ was constant below ca. 40 v/o of the liquid phase. The value of $\Delta S_m$ lowered to the 20 v/o of that in the bulk state for the system containing the powder of which the specific surface area is 25.3 m$^2$/g. It is suggested that the phase transition of the liquid phase near the solid phase was hindered, and the extent of structural

![Figure 5. Variations of $\Delta S_m$ with the hydrate content for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders/ $\text{CaCl}_2\cdot6.00\text{H}_2\text{O}$ coexisting systems.](image)
change depends on the distance from the powder surface.

Under solidification, CaCl2·7.35H2O immediately gives two phases, i.e., CaCl2·6.00H2O crystalline hydrate and saturated CaCl2 aqueous solution. Therefore, the endothermic peak of melting was observed at two temperatures. For the bulk system, these two peaks appear at -51°C, corresponding to a eutectic melting temperature for the mixture of ice and CaCl2·6H2O, and 27°C, corresponding to an end point of melting for the hydrate. The DSC curves for α-Al2O3 (no. 9) powder/ CaCl2·7.35H2O coexisting system are shown in Figure 6. The endothermic peaks were observed at ca. -60°C and 25°C. Both temperatures were lower than those in bulk state. The endothermic peak area at ca. 25°C proportionally increased with the hydrate content. However, the shift of the endothermic peak with the liquid content was observed only for the peak at -60°C, whereas that was barely observed for the peak at 25°C.

It is well-known that aluminum oxide has a hydrophilic surface and whereas silicon carbide has a hydrophobic surface. In order to discuss the dependence on the hydrophilicity of the solid surface for the thermal behavior, the DSC curves for α-SiC powder/ CaCl2·6H2O coexisting systems were measured, as shown in Figure 7. The melting point did not vary with the hydrate content. The endothermic peak area proportionally increased with the liquid content. It is suggested that the phase transition of the hydrate near the solid surface was not affected by the solid surface. The variations of ΔHm and ΔSm for α-SiC powder/ CaCl2·6H2O coexisting systems with the liquid content were shown on Figure 8. The values of ΔHm and ΔSm were nearly constant with the content of the liquid phase, and were nearly equal to that of bulk liquid (32.94 kJ·mol⁻¹ and 108.7 J·mol⁻¹·K⁻¹). It suggested that the hydrate was wholly coagulating near the solid phase.

On discussing the relationship between the properties of the hydrate and that of the powder surface, the wettability of the powder with the liquid phase is very important. In general, the hydrophilic property of the surface of the inorganic compound was represented by the heat of immersion as the surface enthalpy or the surface energy. It was reported by some researchers that the heat of immersion by water of α-Al2O3 powder was ranged in 0.9 to 1.2 J·m⁻² (8). On the other hand, that of SiC powder was ranged in 0.3 to 0.6 J·m⁻² (9), which was smaller than that of α-Al2O3 powder. Those results may be the analogous to those for the CaCl2 hydrate as the liquid. If the influence of the solid phase appeared by a contact of the solid phase and liquid one, the wettability remarkably affects on them. Therefore it is suggested that the influence of the solid surface was relatively small for the system containing α-SiC powder. Thus, the phase transition of hydrate near the surface of the solid phase was influenced by the hydrophilicity of solid phase surface.

**Conclusions**

The melting behavior of CaCl2·nH2O coexisting with the inorganic powders was investigated to be measured with differential scanning calorimetry (DSC). For α-Al2O3 powder/ CaCl2·6.00H2O coexisting system, the melting point of the CaCl2·6.00H2O lowered, and ΔHm decreased with both the decreases of the hydrate content and the increase of the specific surface area of the powder. The non-frozen liquid phase was observed near the solid surface. The relationship between the amount of the non-frozen liquid, ϕ_{NFL}, and the electrical conductivity was observed. For α-Al2O3 powder/ CaCl2·7.35H2O coexisting system, the separated solid phase was formed when the hydrate solidified. Two endothermic peaks were observed at ca. -60°C and 25°C. The endothermic peak at 25°C proportionally increased with the liquid content. For α-SiC powder/ CaCl2·6.00H2O coexisting
system, the melting point and the molar enthalpy change of hydrate on melting were constant in the range of 17.2-48.0 v/o of the liquid content. These behaviors showed that the phase transition of hydrate near the surface of the solid phase was influenced by the hydrophilicity of solid surface.

Figure 6. DSC curves for $\alpha$-Al$_2$O$_3$ (no. 9) powder/ CaCl$_2$·7.35H$_2$O coexisting system.

Figure 7. DSC curves for $\alpha$-SiC ($1.1 \text{ m}^3/g$) powder/ CaCl$_2$·6.00H$_2$O coexisting system.
Figure 8. Variations of $\Delta H_m$ and $\Delta S_m$ with hydrate content for $\alpha$-SiC ($1.1 \text{ m}^2/\text{g}$) powder/ CaCl$_2$·6.00H$_2$O coexisting system.

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