Technical Paper

Heat Capacity of Hydrated and Crystalline Aluminas*

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Measurements of high-temperature heat capacity of hydrated and crystalline aluminas such as gibbsite, boehmite, diaspora, tohdite, κ -alumina and α -alumina are reported. The measurements were performed by using a double-adiabatic high-temperature calorimeter with two types of sample container. A closed-type sample container filled with helium gas was used in the temperature range from 310 to 590 K and the reproducibility of the obtained heat capacities was within $\pm 0.5\%$. For the higher temperature measurements an open-type sample container was used and the reproducibility of the data, at temperatures between 380 and 1,100 K, was $\pm 1.5\%$. The heat capacity equations were derived from the experimental data.

1 Introduction

Crystalline Alumina and hydrated alumina are known to have several structural modifications or hydrated forms, and the accurate knowledge of their thermodynamic properties at high temperatures is an apparent desideratum for both scientific and industrial respects.

Among the modifications of crystalline alumina, which are denoted as α , γ , δ , κ , ρ , η and χ , only α -alumina has been studied extensively on its thermodynamic properties. Its heat capacity at temperatures from 14 to 1,200 K was determined by Ginnings and Furukawa¹⁾ quite accurately, and has been used as the standard value for heat capacity measurements. No report has been published, on the other hand, on the heat capacity of alumina in other transition forms.

As for the hydrated aluminas, Shomate and Cook²⁾ reported the heat capacities of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) in the temperature range between 50 and 290 K, and that of diaspora ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) was determined by King and Weller³⁾ in the same temperature range.

The present paper reports on the measurements of high-temperature heat capacities of gibbsite, boehmite, diaspora, tohdite and κ -alumina, together with α -alumina as a standard material, by using a high-temperature, double-adiabatic calorimeter.

2 Experimental

2.1 Samples

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The samples used were as follows :

(i) α -alumina ($\alpha\text{-Al}_2\text{O}_3$); synthetic sapphire prepared by the U.S. National Bureau of Standards as a standard material for heat capacity measurements.

(ii) Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$); recrystallized at 80°C in a sodium aluminate solution which was prepared with 99.99% pure metallic aluminium and GR-grade sodium hydroxide.

(iii) Boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$); prepared by a hydrothermal treatment of gibbsite in an autoclave at 300°C for 2 hr.

(iv) Diaspora ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$); prepared by a hydrothermal treatment of boehmite in 0.4% NaOH solution, in which 5% of natural diaspora was added, at 380°C, 500 atm for 1 week.

(v) Tohdite ($\text{Al}_2\text{O}_3 \cdot \frac{1}{5}\text{H}_2\text{O}$); prepared by a hydrothermal treatment of a mixture of 96% fine gibbsite, 2% α -alumina and 2% aluminium fluoride at 500°C, 500 atm for 5 days.

(vi) κ -alumina ($\kappa\text{-Al}_2\text{O}_3$); prepared by dehydration of tohdite at 840°C under a vacuum of 10^{-5} torr.

The results of chemical analysis of these samples are listed in Table 1. They were also confirmed by the X-ray analysis.

Table 1 Composition of the samples (wt. %)

		Gibbsite	Boehmite	Diaspora	Tohdite	κ -alumina
Al_2O_3	exp.	65.30	84.00	83.98		
	calc.	65.38	85.00	85.00		
H_2O	exp.	34.30	16.00	14.80	4.00	0.7
	calc.	34.62	15.00	15.00	3.41	
Impurity		Na_2O	Na_2O		$\alpha\text{-Al}_2\text{O}_3^a$	$\alpha\text{-Al}_2\text{O}_3^a$
		0.14	0.16		4.5	4.8

a: Estimated from X-ray analysis

2.2 Apparatus

The calorimeter used is of a high-temperature dou-

ble adiabatic control type, originally designed and manufactured by Shimazu Seisakusho Co.⁹. The main body of the calorimeter consists of a sample container, an inner furnace, an inner thermal shield, an outer furnace, and three outer thermal shields. The silver sample container is surrounded by the egg-shell type beryllia inner furnace for which Kanthal wire is used as a heater and the inner thermal shield made of silver is fitted in the inner furnace. The temperature difference between the sample container and the inner thermal shield was controlled within $\pm 0.05^\circ\text{C}$ below 600 K and $\pm 0.2^\circ\text{C}$ up to 1,100 K by a PID-type controller. The outer furnace made of nickel and three outer thermal shields are placed outside the inner furnace. The temperature difference between the inner and outer furnaces was controlled by another PID-type controller.

Two types of the sample container were used in this study. The one is of closed-type, made of silver and has a capacity of 8 cm³. This was used for the measurements in the temperature range from 310 to 590 K. Helium gas (20 torr) was employed to enhance thermal contact. To ensure vacuum-tightness, a fluorine synthetic rubber "Viton" gasket was used. The other is of an open-type, made of silver, and was used for the measurements in the temperature range between 380 and 1,100 K.

The sample heater, 0.2 mm in diameter Kanthal wire, was wound non-inductively on a quartz tube. Its resistivity was about 15 Ω . The heater assembly was inserted into a hole in the center of the container. The electric power to the sample heater was supplied and controlled by a constant current circuit. The current was detected by a D.C. potentiometer.

The temperature rise of the sample and the temperature difference between the inner and outer furnace were detected by 0.2 mm in diameter alumel-chromel thermocouples manufactured by Hoskins manufacturing Co.

2.3 Procedure

The heat capacity measurements were performed under a vacuum of 3×10^{-5} torr by a continuous heating method, and the optimum heating rate was about $2^\circ\text{C}/\text{min}$ for the sample container of closed-type and $1.1 \sim 1.4^\circ\text{C}/\text{min}$ for that of open-type. The sample was heated up continuously by a constant electric current, and the heat capacity was calculated by measuring the time required to raise the temperature of the sample and the container assembly by the amount equivalent to an electromotive force of 800 μV from the thermocouple. The heating energy supplied to the sample and the container assembly was calculated precisely from the current which was measured from time to time and from the known resistivity of

the sample heater and its temperature dependence.

3 Results

3.1 Data obtained by the closed-type sample container

The experimental results of heat capacity of α -alumina, obtained by using the closed-type sample container, were presented in Table 2 together with the N.B.S. standard values¹⁰. The experimental values, which were calculated from the gross heat capacity of α -alumina with sample container by subtracting that of the empty container, were apparently 1~2% higher than the standard values¹⁰. This can be ascribed that when the sample container is filled with the sample, the heat leak will be slightly higher than the case of the empty container. Therefore, the "apparent" heat capacity of the empty container assembly, which included the loss through heat leak, was determined from the measured gross heat capacity of the sample container filled with α -alumina, by subtracting the net heat capacity of α -alumina calculated from the N.B.S. standard data.

Table 2 Heat capacities of α -alumina and hydrated aluminas

T (K)	C_p (cal mol ⁻¹ K ⁻¹)				
	α -alumina		Gibbsite $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Boehmite $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Diaspore $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	measured	std. value			
312.8	20.0	19.62	45.6	32.8	26.0
332.3	20.9	20.53	47.4	34.0	27.2
351.5	21.6	21.29	49.2	35.4	28.0
370.6	22.0	22.01	50.8	36.8	29.5
390.0	22.8	22.68	52.5	37.9	30.7
409.8	23.4	23.27	53.7	39.0	32.0
429.8	23.8	23.81	55.2	40.0	33.1
449.5	24.5	24.29	56.6	41.4	34.1
469.3	25.0	24.73		42.7	35.0
489.1	25.2	25.14		43.8	35.8
508.7	25.7	25.50		44.7	36.5
528.2	25.9	25.84		45.7	37.5
547.4	26.3	26.15		46.5	38.0
566.5	26.6	26.42		47.2	39.0
585.7	26.8	26.70		48.0	39.5

The obtained heat capacities of gibbsite, boehmite and diaspora are presented in Table 2. The experimental values were reproducible within $\pm 0.5\%$ in the temperature range from 310 to 590 K.

3.2 Data obtained by the open-type sample container

Heat capacities of α -alumina and tohdite were measured by using the open-type sample container in the temperature range between 380 and 1,100 K. The

heat capacity of the standard sample of α -alumina was also measured in the same temperature range and the results were used to obtain the "apparent" heat capacity of the empty sample container, in the same way as described in the previous section. Although the heat leak was fairly large as compared with the results obtained by the closed-type container, the reproducibility of the data was within $\pm 1.5\%$ up to 1,100 K.

The obtained heat capacities are presented in Table 3. As tohdite starts to dehydrate above 800 K, its heat capacity was measured up to this temperature.

Table 3 Heat capacities of κ -alumina and tohdite

T (K)	C_p (cal mol ⁻¹ K ⁻¹)		T (K)	C_p (cal mol ⁻¹ K ⁻¹)	
	κ -alumina κ -Al ₂ O ₃	Tohdite Al ₂ O ₃ · 1/5 H ₂ O		κ -alumina κ -Al ₂ O ₃	Tohdite Al ₂ O ₃ · 1/5 H ₂ O
380.5	23.0	23.6	767.4	29.1	32.6
400.0	23.1	24.4	786.3	29.3	32.9
420.0	23.9	25.2	805.0	29.3	
440.0	24.8	26.0	823.7	29.6	
460.0	25.0	26.5	842.4	29.7	
480.0	25.5	27.0	861.2	29.7	
500.0	25.9	27.5	880.0	30.0	
519.0	26.3	27.7	898.7	29.9	
539.0	26.6	28.4	917.6	30.1	
558.4	26.9	28.6	936.6	30.2	
577.8	27.1	29.3	955.7	30.2	
597.0	27.5	29.6	974.7	30.6	
616.2	27.8	29.5	993.8	30.9	
635.2	28.0	30.0	1012.8	30.8	
654.3	28.2	30.5	1031.9	30.8	
673.4	28.4	30.8	1051.3	30.9	
692.3	28.5	31.3	1070.8	31.2	
711.2	28.7	31.3	1090.3	31.2	
730.0	29.1	31.7	1109.9	31.2	
748.7	29.2	32.2			

4 Discussion

The heat capacity equations were derived from the obtained data by using a least squares method. The results are summarized as follows (C_p in cal. mol⁻¹. K⁻¹);

$$\text{gibbsite: } C_p = 38.99 + 4.83 \times 10^{-2} T - 8.36 \times 10^5 T^{-2} \quad (300-450 \text{ K})$$

$$\text{boehmite: } C_p = 25.81 + 4.14 \times 10^{-2} T - 6.01 \times 10^5 T^{-2} \quad (300-590 \text{ K})$$

$$\text{diaspore: } C_p = 23.65 + 3.12 \times 10^{-2} T - 7.55 \times 10^5 T^{-2} \quad (300-590 \text{ K})$$

$$\text{tohdite: } C_p = 24.62 + 1.19 \times 10^{-2} T - 7.83 \times 10^5 T^{-2} \quad (380-790 \text{ K})$$

κ -alumina:

$$C_p = 28.06 + 0.36 \times 10^{-2} T - 9.77 \times 10^5 T^{-2} \quad (380-1,100 \text{ K}).$$

These derived equations are shown by full lines in Figs. 1 and 2. The experimental data points are also plotted to show the deviations from the equations. In Fig. 1, the available data for lower temperatures

Fig. 1 Heat capacities of α -alumina and hydrated aluminas

Fig. 2 Heat capacities of κ -alumina and tohdite