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Kinetics on the Formation and Decomposition of $2Al_2O_3 \cdot B_2O_3$ from Mixed Powders Prepared by the Alkoxy-method

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Synopsis. The formation of the alkoxy-derived $2Al_2O_3.B_2O_3$ was observed in the temperature range 820—930 °C. Crystallization isotherms were best described by the contracting cube equation, the activation energy being determined as 368 kJ/mol. The kinetics on the decomposition of $2Al_2O_3.B_2O_3$ was also studied.

Aluminum boron oxide is known to exist in three forms, $9Al_2O_3 \cdot 2B_2O_3$ (orthorhombic), $2Al_2O_3 \cdot B_2O_3$ (orthorhombic), and $Al_2O_3 \cdot B_2O_3$ (hexagonal).[1-7] The former two can be prepared by the solid-liquid reaction from oxide mixtures, such as the system $\alpha \cdot Al_2O_3$–B_2O_3,[2] $\gamma \cdot Al_2O_3$–B_2O_3,[5] and $Al(OH)_3$–H_3BO_3.[3] The last one $Al_2O_3 \cdot B_2O_3$ has been recognized as a mineral, jeremejective. In a previous paper[8] dealing with the formation of $9Al_2O_3 \cdot 2B_2O_3$ from the mixed powders prepared by the simultaneous hydrolysis of aluminum and boron alkoxides, it was shown that the reaction process is similar to that of mullite($3Al_2O_3 \cdot 2SiO_2$) formed by heating a clay mineral, kaolinite($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Several investigators[2,5,6] reported that $2Al_2O_3 \cdot B_2O_3$ melts incongruently at 1030—1050 °C to $9Al_2O_3 \cdot 2B_2O_3$ and liquid. No kinetic study, however, has been carried out. The present study is concerned with the kinetics of the formation and decomposition of the alkoxy-derived $2Al_2O_3 \cdot B_2O_3$.

Experimental

Boron triethoxide of guaranteed purity was used. Aluminum tris(isopentyl oxide) was synthesized by heating aluminum metal in an excess isopentyl alcohol with a small amount of mercury(II) chloride as a catalyst at 130 °C for 7 h.[9] Aluminum metal of purity 99.9% was used. A mixture of these alkoxides in the mole ratio $Al^{3+}/B^{3+}=2:1$ was prepared, and then poured into aqueous ammonia solution at 30 °C. The resulting mixed powders were washed with hot water and dried at 60 °C under reduced pressure. The average particle size of the mixed powders is *ca.* 550 Å. The X-ray diffraction(Cu $K\alpha$) pattern(Fig. 2(a)) is similar to that of the mixture whose Al^{3+}/B^{3+} mole ratio is 9:2. In view of the previous study,[8] the mixed powders are considered to be B^{3+}-substituted boemite(AlO(OH)) gel.

Results and Discussion

The TG of the mixed powders was carried out in the air from room temperature to 1000 °C(Fig. 1). The weight loss of 20.1% up to 710 °C is attributed to the loss of ammonia, absorbed water, hydrated water constitution water, and organic residue from the parent alcohol. DTA was also studied. Exothermic and endothermic reactions were observed at 820—930 °C and 1030—1250 °C, respectively. From the results of X-ray diffraction, the reactions were found to be the crystallization of $2Al_2O_3 \cdot B_2O_3$ from an amorphous phase and the decomposition of $2Al_2O_3 \cdot B_2O_3$ into $9Al_2O_3 \cdot 2B_2O_3$ and liquid, respectively.

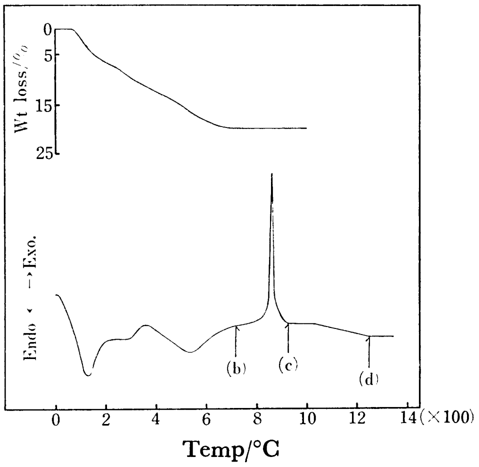

Fig. 1. TG and DTA curves of mixed powders as a raw material. Sample weight: 20 mg, heating rate: 10 °C/min.

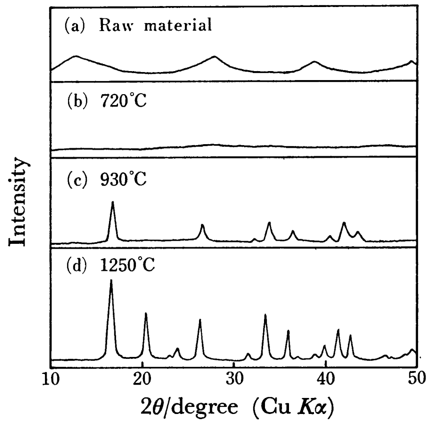

Fig. 2. X-Ray diffraction patterns of specimens with increasing temperature.
Heating rate: 10 °C/min.
(a) B^{3+}-substituted AlO(OH) gel, (b) amorphous material, (c) $2Al_2O_3 \cdot B_2O_3$, (d) $9Al_2O_3 \cdot 2B_2O_3$.

Figure 2 shows the variation of X-ray diffraction patterns of specimens with increasing temperature. The specimen heated at 720 °C after the completion of weight loss was amorphous, no significant changes being observed at 800 °C. The peaks corresponding to $2Al_2O_3 \cdot B_2O_3$ appeared at 820 °C for 25 min, the intensity increasing with increasing temperature and time. No other peaks were identified except for the $2Al_2O_3 \cdot B_2O_3$ spectrum up to 1000 °C. The peaks of $9Al_2O_3 \cdot 2B_2O_3$, as the decomposition product of

$2Al_2O_3 \cdot B_2O_3$, began to appear at 1030 °C. The specimen heated at 1250 °C showed the X-ray diffraction pattern of only $9Al_2O_3 \cdot 2B_2O_3$.

Figure 3 shows the fraction of the $2Al_2O_3 \cdot B_2O_3$ crystallization at 820, 840, and 870 °C. The mixed powders were pre-heated at 720 °C for 15 min. The average particle size of the specimen was 0.12 μm. The fraction of crystallization of each specimen was determined from the height of $d=5.29$ Å$(2\theta=16.7°)$ which is the strongest line of the $2Al_2O_3 \cdot B_2O_3$ spectrum. A well-crystallized specimen was obtained by heating the mixed powders at 950 °C for 30 min. Calcium fluoride was used as a standard material. Induction periods were observed, attempts being made to fit the results to kinetic laws by considering the induction periods. As shown in Fig. 4, crystallization isotherms are best described by the contracting cube equation $1-(1-\alpha)^{1/3}=k(t-t_0)$,¹⁰⁾ where α is the fraction of crystallization, t time and t_0 induction period. This indicates that the rate of crystallization is controlled by the rate of advance of the reaction interface. The rate constants were determined from the slopes of straight lines. The value of the activation energy calculated from the Arrhenius plot was 368 kJ/mol.

Figure 5 shows the fraction of decomposition of $2Al_2O_3 \cdot B_2O_3$ into $9Al_2O_3 \cdot 2B_2O_3$ and liquid as a function of time at different temperatures. The specimen heated at 950 °C for 30 min was used as a starting material. The fraction of decomposition of each specimen was determined by comparing the height of the $d=4.35$ Å $(2\theta=20.4°)$ line with that of the same line of a fully decomposed specimen, $9Al_2O_3 \cdot 2B_2O_3$. The data can be interpreted in terms of the second-order equation, as a special case of the treatment by Avrami¹¹⁾ and Czanderna *et al.*¹²⁾ Figure 6 shows the plots of $f/1-f$ against t, where f is the fraction decomposed in time t. The activation energy was 301 kJ/mol, representing that employed for establishing active growth centers.

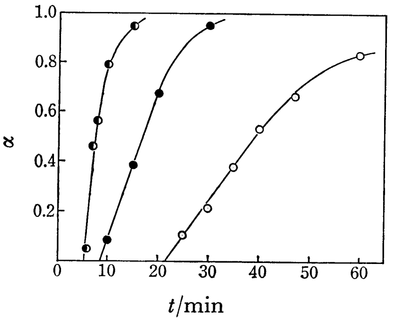

Fig. 3. Formation of $2Al_2O_3 \cdot B_2O_3$ as a function of time at different temperatures. ○: 820 °C, ●: 840 °C, ◐: 870 °C.

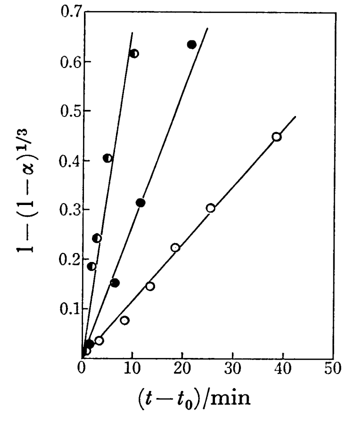

Fig. 4. Plots of $1-(1-\alpha)^{1/3}$ *vs.* time $t-t_0$ of the data shown in Fig. 3. ○: 820 °C, ●: 840 °C, ◐: 870 °C.

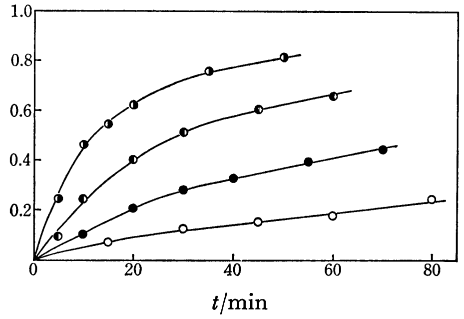

Fig. 5. Decomposition of $2Al_2O_3 \cdot B_2O_3$ as a function of time at different temperatures. ○: 1000 °C, ●: 1050 °C, ◐: 1100 °C, ◑: 1150 °C.

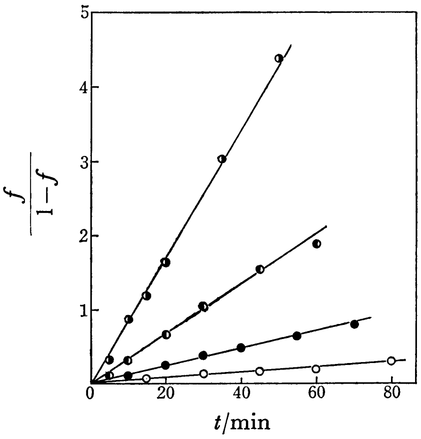

Fig. 6. Second-order plots of the data shown in Fig. 5. ○: 1000 °C, ●: 1050 °C, ◐: 1100 °C, ◑: 1150 °C.

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