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Effects of Sodium Tetraborate as an Additive on the Reaction of α-Alumina with Sodium Carbonate

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Effects of sodium tetraborate as an additive in the reaction of α-alumina with molten sodium carbonate have been studied mainly in a N_2 atmosphere. Addition of sodium tetraborate accelerates the reaction, the α-alumina reacted increasing from 31.7% to 99.3% by addition of sodium tetraborate corresponding to the initial B_2O_3/Na_2O molar ratio of only 1/15 under the other same conditions. By means of the Jander equation the activation energy was found to be 53 kcal/mol for the α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system, which was lower by 10 kcal/mol than that for the α-Al_2O_3–Na_2CO_3 system. X-Ray diffraction and thermal data were analyzed in relation to the phase equilibrium of the melt.

Production of alumina from resources other than bauxite is becoming important. A number of reports have appeared on the production of alumina from various low-grade sources such as clay, aluminous shale, anorthosite, nephelite, *etc.*[1-8]

A lime-soda sinter process is one of the most important methods for extracting alumina from low-grade sources to which the Bayer process can not be applied because of high silica content. Raw materials reacted with molten sodium carbonate form sodium aluminate which is soluble in both acidic and basic aqueous solutions. The reaction of various types of alumina with sodium carbonate is fundamental in the complex lime-soda sinter process.

In a previous paper the lime-soda sinter process was discussed with use of Korean diaspore, cyanite and kaolinite as starting materials.[9] Christie *et al.* studied the reaction rate of α-alumina with sodium carbonate in relation to gasification of coal in melts containing sodium carbonate, showing that the reaction process is considerably hindered by diffusion.[10]

Sodium tetraborate is often used as a flux for the decomposition of minerals by molten Na_2CO_3. The purpose of the present work is to clarify the promoting action of sodium tetraborate on the reactivity of α-alumina with sodium carbonate.

Experimental

Reagent grade α-alumina was ground and sized into −150—+200 mesh (No. 1) and −200 mesh (No. 2). The specific surface area of No. 2 was found to be 0.90 m^2/g by the BET method. Reagent grade anhydrous sodium carbonate and sodium tetraborate decahydrate (borax) were dried at 500 °C for 1 h. Nitrogen and oxygen were purified by the usual methods. Other materials were of reagent grade and used without further purification.

The percentage of α-alumina reacted with sodium carbonate, η, was determined as follows: Samples in a platinum boat were laid in an electric furnace at 900—1250 °C. The sinter was cooled down to room temperature as fast as possible in N_2 gas, and leached with hot 1 mol/dm³ HCl solution for 30 min. The leachate was filtered. $Al(OH)_3$ was precipitated by adding aqueous ammonia to the filtrate and weighed in the form of Al_2O_3 after heating. The value of η was calculated from the weight of alumina leached.

Results and Discussion

Effect of Gas Atmosphere. α-Alumina reacts with sodium carbonate to form sodium aluminate:

$$Al_2O_3(s) + Na_2CO_3(l) = 2NaAlO_2(s) + CO_2(g). \quad (1)$$

From the large negative value of Gibbs free energy for this reaction[11] α-alumina is expected to react completely with molten Na_2CO_3 at temperatures above 900 °C. However, the experimental results (Fig. 1) indicate that the reaction is not complete in the air. For example, the value of η was found to be low at 66% even for the initial molar ratio(m) 5 of Na_2CO_3/Al_2O_3 and reaction time 5 h at 1250 °C. The sinters obtained in the air were colored brown, the Pt boat containing the sinter being considerably corroded. In spite of the disappearance of α-alumina in X-ray diffraction patterns of the sample sintered for a long time, the value of η was much lower than 100% (Fig. 3a).

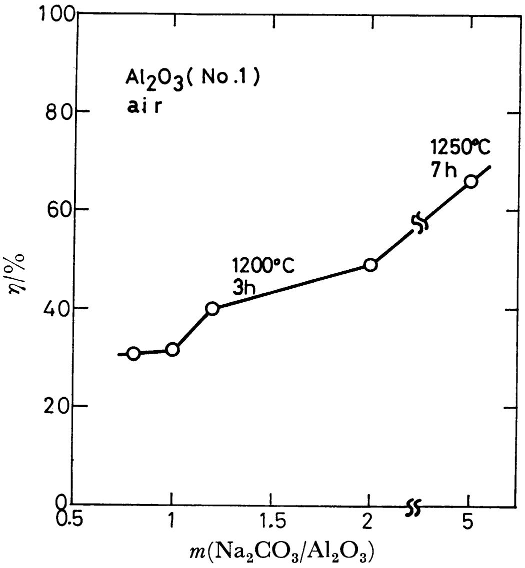

Fig. 1. Variation of the percents of α-alumina reacted with initial Na_2CO_3/Al_2O_3 molar ratio.

Maegawa found that the atmosphere influences the sintering process, and that H_2O gas atmosphere enhances the rate of reaction of α-alumina with sodium carbonate in comparison with O_2, H_2+CO, or CO_2 gas atmos-

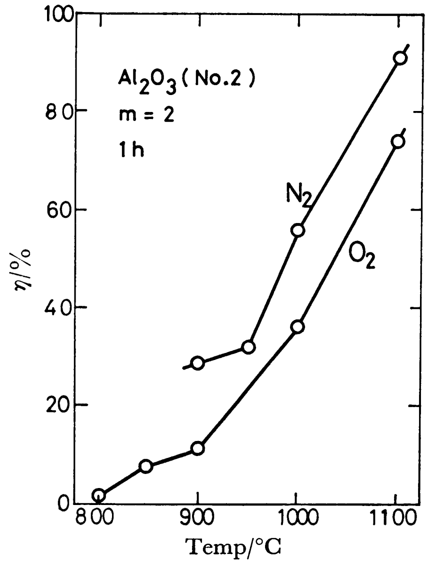

Fig. 2. Difference between the effect of N_2 and O_2 gas atmospheres on the reaction of Al_2O_3 with Na_2CO_3.

phere.[12] Figure. 2 shows changes in the η values with reaction temperature in purified N_2 and O_2 with constant flow rates of 80 ml/min. The values of η obtained in O_2 were found to be lower than those obtained in N_2, the corrosion of the Pt boat being much enhanced in O_2. The sinter obtained in N_2 remained white with no corrosion of the Pt boat; those obtained in O_2 were colored red-brown as in the air. The same results were obtained when a Ni boat was used. By comparing Fig. 3a with 3b, we see that there are compounds other than α-Al_2O_3(a), Na_2CO_3(n), and $NaAlO_2$(na). Carbon dioxide,[10] as well as O_2 seems to hinder the sinter process.

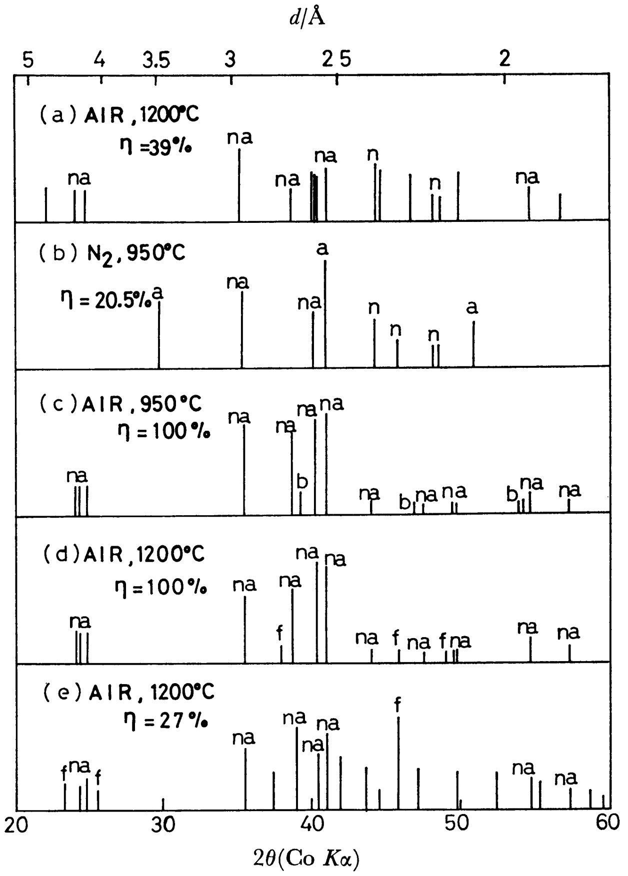

Fig. 3. X-Ray diffraction data for the sinters obtained under conditions as follows: (a) α-Al_2O_3 (No.1)+Na_2CO_3, $m=5$ (b) α-Al_2O_3 (No. 1)+Na_2CO_3, $m=2$ (c) α-Al_2O_3 (No.1)+Na_2CO_3+$Na_2B_4O_7$, $m=1.7$ and $n=1/15$ ($X_{B_2O_3}=0.053$) (d) α-Al_2O_3 (No. 1)+Na_2CO_3+AlF_3 (20 wt%), $m=2$ (e) α-Al_2O_3 (No. 1)+Na_2CO_3+AlF_3 (20 wt%), $m=1$, 1 Å=0.1 nm.

Effect of Additives. Sodium tetraborate and aluminium fluoride were used as additives to facilitate Reaction 1. Addition of sodium tetraborate was found to be very effective (Fig. 4). The greater the initial

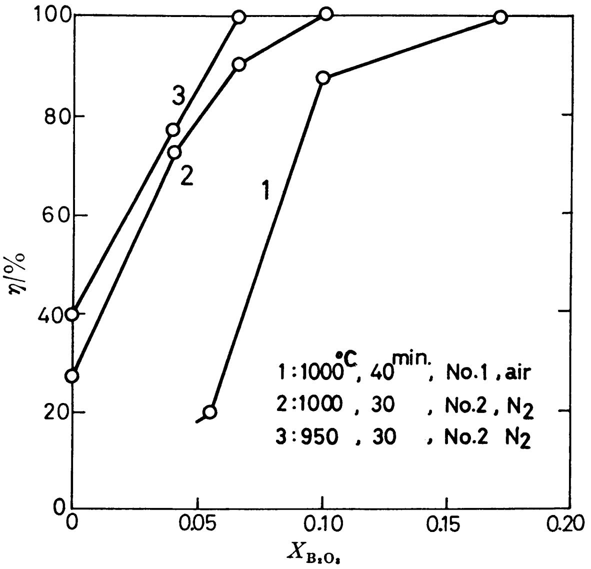

Fig. 4. Effect of the addition of borax on the reaction of α-Al_2O_3 with Na_2CO_3.

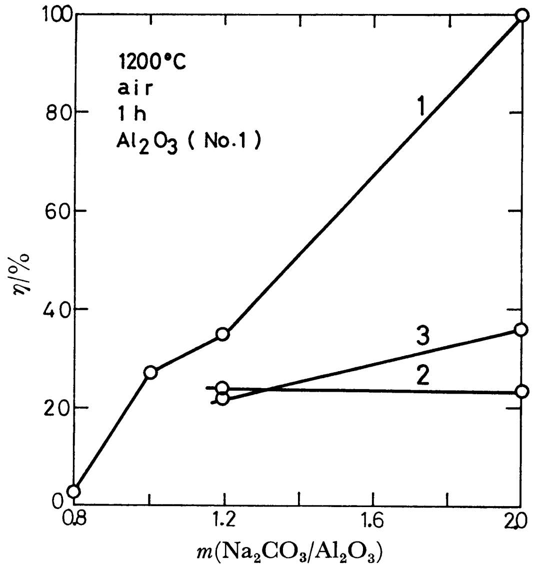

Fig. 5. Effect of the addition of AlF_3 and NaF on the reaction of Al_2O_3 with Na_2CO_3.
Curve 1; α-Al_2O_3+Na_2CO_3+AlF_3 (20 wt%), 2; α-Al_2O_3+Na_2CO_3+NaF(20 wt%), 3; α-Al_2O_3+Na_2CO_3.

B_2O_3/Na_2O molar ratio(n), the greater the effect. The sinters to which sodium tetraborate had been added remained white, causing no corrosion of the Pt boat. The sinter having $\eta=100\%$ obtained for the Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system gave only the diffraction patterns of $NaAlO_2$ and probably sodium borate(b) (Fig. 3c).

The effects of AlF_3 and NaF as additives were also studied. The effect of AlF_3 on Reaction 1 depends a great deal on the value of m (Fig. 5). When 20 wt% AlF_3 was added to a mixture with m of 2.0, the value of η increased from 36% to 100%. Aluminium fluoride reacts with molten Na_2CO_3 partly to form $NaAlO_2$:

$$AlF_3 + 2Na_2CO_3 = 3NaF + NaAlO_2 + 2CO_2, \quad (2)$$

$$AlF_3 + 3NaF = Na_3AlF_6. \quad (3)$$

If all the AlF_3 added were converted into NaF, the effect of NaF would be observed similar to that of AlF_3. However, this was not the case (Fig. 5). X-Ray diffraction analysis of the sinter obtained in the case of $m=2$ and $\eta=100\%$ showed the presence of $NaAlO_2$ and a fluoride compound(f), probably Na_3AlF_6. In the case of $m=1$ and $\eta=27\%$, η was found to be low, in spite of the absence of the diffraction pattern for α-Al_2O_3. This suggests that α-Al_2O_3 might merely dissolve in Na_3AlF_6 formed by the reaction of AlF_3 with Na_2CO_3.

Reaction Rate as a Function of Temperature. Figures 6 and 7 show changes in η with reaction time, t, at three temperatures for α-Al_2O_3–Na_2CO_3($m=2$) and α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$($m=2$ and $n=1/15$).

Since a protective layer of sodium aluminate having very low solubility in molten Na_2CO_3,[10] is formed on alumina, the diffusion of CO_3^{2-} ion through the sodium aluminate layer would be the rate-determining step.[10,12] The results were analyzed by means of the Jander equation

$$[1-(1-\eta)^{1/3}]^2 = kt, \quad (4)$$

$$k = \frac{2DC_0}{\rho r_0^2}, \quad (5)$$

where k is a rate constant, D diffusion coefficient, C_0 the concentration of CO_3^{2-} ion in the bulk, ρ is the density of $NaAlO_2$ layer (2.72 g/cm^3), and r_0 the average size of α-Al_2O_3 (0.28 μm) calculated from the special area of 0.09 m^2/g. Figures 8 and 9 show linear relationships,

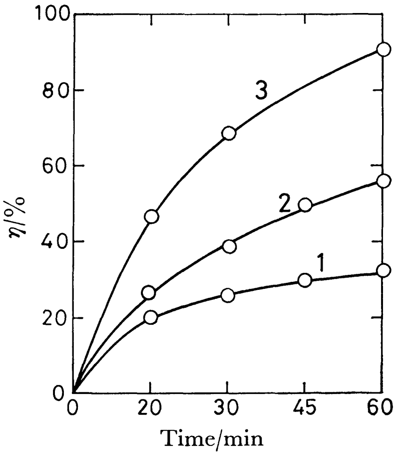

Fig. 6. Changes in the percents of α-alumina reacted *vs.* time in the N_2 atmosphere for α-Al_2O_3–Na_2CO_3 system ($m=2$).
Curve 1: 950 °C, 2: 1000 °C, 3: 1100 °C.

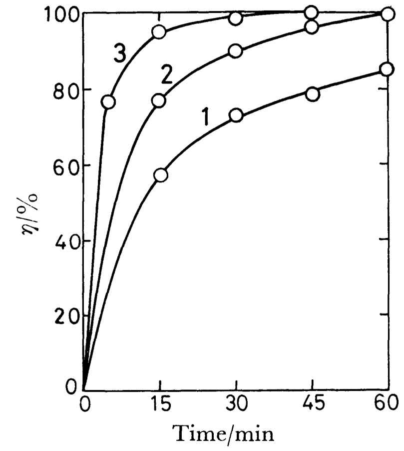

Fig. 7. Changes in the percents of α-alumina reacted *vs.* time in the N_2 atmosphere for α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system ($m=2$, $n=1/15$).
Curve 1: 900 °C, 2: 950 °C, 3: 1000 °C.

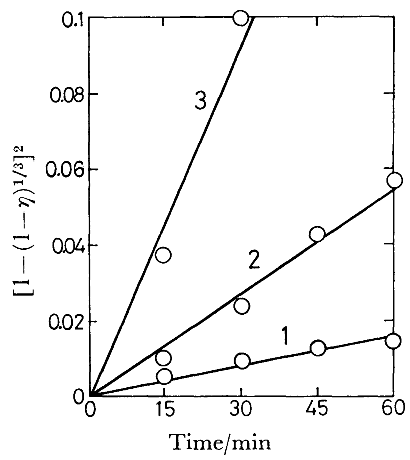

Fig. 8. $[1-(1-\eta)^{1/3}]^2$ *vs.* reaction time for α-Al_2O_3–Na_2CO_3 system.
1: 950 °C, 2: 1000C°, 3: 1100 °C.

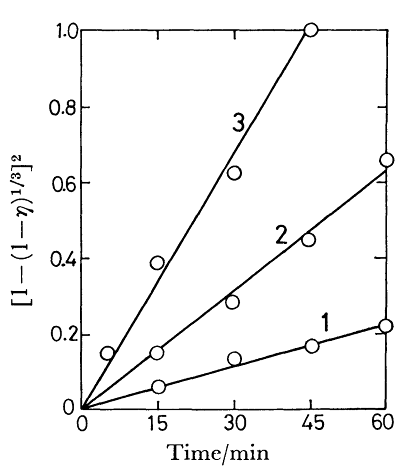

Fig. 9. $[1-(1-\eta)^{1/3}]^2$ *vs.* reaction time for α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system.
1: 900 °C, 2: 950 °C, 3: 1000 °C.

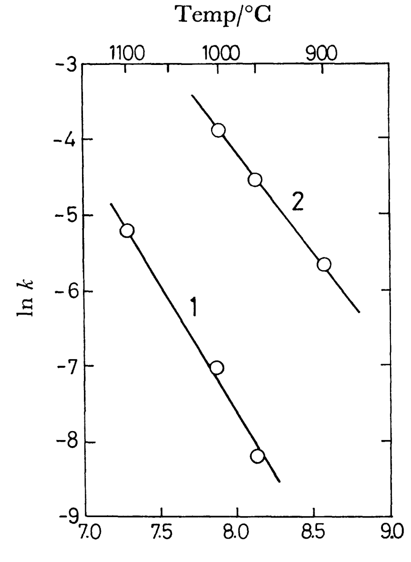

Fig. 10. Variation of rate constant, k, with temperature. 1: α-Al_2O_3–Na_2CO_3 system, 2: α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system.

the slopes giving the k values. At 1000 °C the k value for α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system is larger by *ca.* 11 times than that for α-Al_2O_3–Na_2CO_3 system. Figure 10 shows Arrhenius-type plots of k *vs.* $10^4/T$. The activation energy calculated from the slopes is 53 kcal/mol for the former, lower by 10 kcal/mol than that for the latter (kcal means $kcal_{th}$; 1 $kcal_{th}$=4184 J). For the Arrhenius activation energy for the reaction of α-Al_2O_3 with Na_2CO_3, Christie *et al.*10) and Maegawa *et al.*12) reported the values of 62±3 and 58.8 kcal/mol, respectively, which agree with our results.

Discussion on the Effect of Sodium Tetraborate as an Additive. Molten Na_2CO_3 is completely ionized and consists of species such as Na^+, CO_3^{2-}, and ion pair $(Na^+CO_3^=)^-$, the dissociation of CO_3^{2-} into CO_2 and O^{2-} ion being finite at temperatures above melting point.13) Thus the reaction of α-alumina with Na_2CO_3 can be expressed by a series of elementary steps as follows:

$$Na_2CO_3(l) = Na^+(l) + (Na^+CO_3^=)^-(l), \quad (6)$$

$$(Na^+CO_3^=)^-(l) = Na^+(l) + CO_3^{2-}(l), \quad (7)$$

$$CO_3^{2-}(l) = O^{2-}(l) + CO_2(g), \quad (8)$$

$$Al_2O_3(s) + O^{2-}(l) = 2AlO_2^-(l), \quad (9)$$

$$Na^+(l) + AlO_2^-(l) = NaAlO_2(s). \quad (10)$$

According to the Lux-Flood concept of basicity of oxides,14,15) a base is defined as an oxide donor and an acid as an oxide acceptor:

$$(\text{acid}) + O^{2-} = (\text{base}) \quad (11)$$

The reaction of α-alumina with sodium carbonate might be the neutralization between acidic Al_2O_3 and basic Na_2O. Thus pO^{2-}[*i.e.* $-\log a(O^{2-})$] was chosen as a scale of basicity. According to the calculation of the relative basicity of oxides by Yagisawa *et al.*, B_2O_3 is more acidic than Na_2O and Al_2O_3.16) Duffy and Ingram,17) who presented a concept of optical basicity for the melt, reported that an increase in B_2O_3 content lowers the basicity of Na_2O–B_2O_3 melt; B_2O_3 has a tendency to consume O^{2-} ion:

$$B_2O_3 + 5O^{2-} = 2BO_4^{5-} \quad (12)$$

It is thus concluded that the effect of the addition of sodium tetraborate is not caused by the increase in the basicity of the melt.

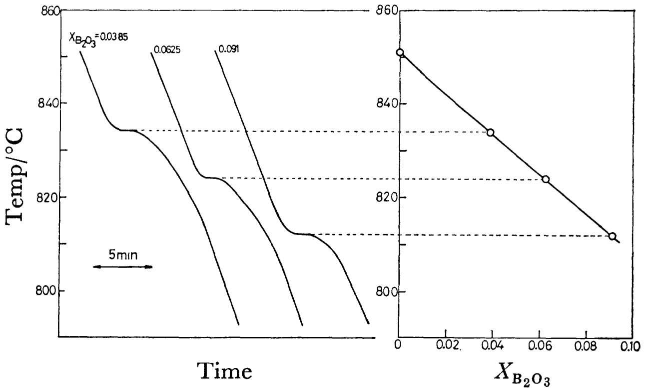

Fig. 11. Cooling curves for mixed melts of Na_2CO_3 and $Na_2B_4O_7$, and the melting points *vs.* $X_{B_2O_3}$.

The phase diagram of Na_2O–B_2O_3 system has been reported only for the region $B_2O_3 \geq 50\%$.18) Basic sodium borates such as $5Na_2O \cdot B_2O_3$, $2Na_2O \cdot B_2O_3$, and $3Na_2O \cdot B_2O_3$ are known in the region $B_2O_3 \leq 50\%$. Figure 11 shows cooling curves for Na_2CO_3–$Na_2B_4O_7$ melts. Addition of sodium tetraborate to sodium carbonate give rise to the lowering of solidification point of the melt in proportion to the molar fraction of B_2O_3. With the progress of Reaction 1, the concentration of B_2O_3 in the melt increases as a result of consumption of Na_2CO_3, lowering the melting point; the nearer the reaction approaches 100% completion, the greater the lowering in melting point. The activation energy for diffusion is approximately proportional to melting point.19) The activation energy for the α-Al_2O_3–Na_2CO_3–$Na_2B_4O_7$ system, having lower melting points, was found to be lower by 10 kcal/mol than for the α-Al_2O_3–Na_2CO_3 system. The lowering of the melting point results in the lowering of the viscosity of the melt, promoting the contact of α-alumina with the melt and the diffusion of CO_3^{2-} and/or $(Na^+CO_3^=)^-$ ion(s) through a porous layer of $NaAlO_2$ formed on the surface of α-alumina.

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