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Promotion of $ZnAl_2O_4$ formation by LiF

Part 1 *Effect of alumina and compaction pressure on zinc aluminate formation in the presence of lithium fluoride*

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The formation of $ZnAl_2O_4$ in the presence of LiF was affected by the various states of Al_2O_3 and by the compaction pressure. The rate curves showed a typical sigmoid form and were analysed by the Hancock and Sharp method. The results indicated the presence of a main process controlled by nucleation which is followed by a diffusion-controlled process. The effects of the aggregation or agglomeration state of Al_2O_3 powder were examined with various Al_2O_3 powders, with compaction pressures of up to 60 MPa on the sample pellets. The amount of $ZnAl_2O_4$ decreased with an increase in the degree of agglomeration or aggregation when the firing temperature was around 600° C, but no effect was observed at higher temperatures. Similar effects were also observed for the compaction pressures. These effects are interpreted as the results of the degree of formation of a liquid intermediate phase.

1. Introduction

In a powdered solid-state reaction, inhomogeneity in the mixed state [1–5] and also the packing state [6, 7] are the important factors affecting the reaction rate. The authors [8] have reported the effect of lithium fluoride on the formation of zinc aluminate from coarse and dense alumina and fine zinc oxide powders. The observation of microstructures indicated the formation of an intermediate phase from the fluoride additive and reactants, leading to the conclusion that the reaction proceeds through the following four steps:

(i) LiF forms an intermediate liquid phase with LiF, ZnO and Al_2O_3.

(ii) Dense $ZnAl_2O_4$ in the ZnO phase is developed by transport of Al_2O_3 through the intermediate phase.

(iii) The dense $ZnAl_2O_4$ layer interrupts the spread of the intermediate phase into the ZnO phase and confines the liquid phase between the $ZnAl_2O_4$ layer and the Al_2O_3 phase. The confined intermediate liquid phase reacts with Al_2O_3 and forms $LiAl_5O_8$.

(iv) Further dissolution of Al_2O_3 by the intermediate phase promotes the growth of $LiAl_5O_8$ and the migration of the liquid phase to the centre of the Al_2O_3 particles.

In order to elucidate the mechanism of $ZnAl_2O_4$ formation in the presence of fluoride additives and to obtain reliable and reproducible kinetic data for the reaction, it is necessary to examine the effects of the physical nature of the starting materials and the geometrical configuration of powders for the reaction. These physical states of powders affect the inhomogeneity in samples which is introduced by the use of different raw materials with different degrees of aggregation or agglomeration of powders, and also affect the packing state which is changed by the compaction pressure on the sample pellets. The purpose of this paper is to investigate the effects of Al_2O_3 with different degrees of aggregation or agglomeration, and the effects of compaction pressure, on zinc aluminate formation in the presence of lithium fluoride.

2. Experimental procedure

2.1. Materials

Four types of alumina from commercial products as starting materials were used: (A, B) two kinds of reagent-grade alumina from the Nakarai Chemical Co., Kyoto 604, Japan, in different aggregated states; (C) electrofused alumina from the Fujimi Kenma Co., Nagoya 452, Japan, which has neither aggregation nor agglomeration; and (D) Alcoa A-16 SG from the Aluminum Co. of America, Pittsburgh, Pennsylvania, USA, which forms soft agglomerates. Fig. 1 shows schematically the different states of alumina, i.e. agglomerated, aggregated and electrofused alumina. The states of these aluminas are changed by the factors shown in Fig. 1. X-ray diffraction (XRD) revealed that the crystalline state of all these sources of Al_2O_3 is of the corundum type. Examination of the particle sizes of A, B and C by the optical transmittance method and by electron microscopy were conducted and the sizes of primary particles were determined to be 3.6, 4.4 and 1.8 μm, respectively. Alcoa A-16 SG alumina was an agglomerate and its primary particle size was evaluated to be 0.2 μm by transmission electron microscopy. Zinc oxide was a guaranteed reagent from the Kishida Chemicals Co. The particle size was in the vicinity of 0.3 μm. Lithium fluoride was an extra-pure reagent from the Nakarai Chemicals Co.

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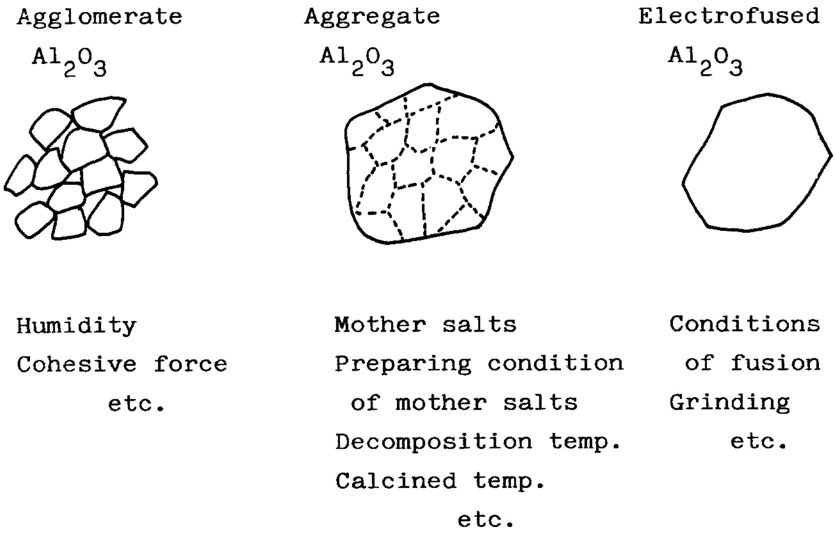

Figure 1 Scheme of various physical states of alumina powder.

2.2. Sample preparation

Five kinds of reaction specimen designated as Samples I to V, with 20 mol% of lithium fluoride, were prepared by combining equimolar amounts of zinc oxide and alumina from various sources: Sample I had an equiweight mixture of Aluminas A and B; Sample II, small aggregates of Alumina A; Sample III, large aggregate of Alumina B; Sample IV, electrofused Alumina C as purchased, and Sample V, agglomerated Alcoa-A 16 SG alumina. Samples were shaken with glass beads in the dry state. The mixture was compacted in a 10 mm diameter steel die under uniaxial pressures of 15, 30 and 60 MPa. The compacts were fired in an electric furnace at 570 to 900° C for up to 50 h.

2.3. Determination of the extent of $ZnAl_2O_4$ formation and identification of developed phase

The extent of $ZnAl_2O_4$ formation was calculated from the amount of residual ZnO. The latter was determined chemically by dissolving ZnO with 2 mol dm^{-3} HCl solution and titrating Zn^{2+} with 0.01 mol dm^{-3} EDTA solution with EBT (Eriochrome Black T) as the indicator at pH 10. Phases in the fired specimens were indentified by X-ray diffraction (Jeol Model JDX 7E) analysis using conventional techniques.

3. Results and discussion

3.1. Effect of various states of Al_2O_3 on the rate of $ZnAl_2O_4$ formation in the presence of LiF

The effects of various states of Al_2O_3 on $ZnAl_2O_4$ formation in the presence of LiF were examined. Fig. 2 shows the rate curves of Samples I to V fired at 570 and 600° C (Fig. 2a) and at 650 and 700° C (Figs. 2b and c). As seen in Fig. 2a, at low firing temperatures between 570 and 600° C all the rate curves showed an induction time before a rapid increase of $ZnAl_2O_4$ content and changed along a sigmoidal curve to different limits, except for the curve of Sample II fired at 600° C. The shapes of the sigmoidal curves differed from each other with the variation of the source of alumina, in induction period as well as the speed of $ZnAl_2O_4$ formation. On the other hand, when the firing temperature was elevated from 650 to 700° C the amount of $ZnAl_2O_4$ abruptly increased up to a certain limit in an early stage of the reaction without an induction time, and then the reaction did not proceed any more. The limit attained seems constant irrespective of the source of Al_2O_3.

3.2. Analysis of the rate curves obtained at a low firing temperature

The Hancock and Sharp method [9] was applied to analyse the rate curves obtained at low firing temperatures. This method is based on the Avrami–Erofeev equation [10–13], where the extent α of a reaction is expressed by an exponential function of time:

$$\alpha = 1 - \exp(-kt^m) \qquad (1)$$

Taking logarithms of both sides of Equation 1, the following equation is obtained:

$$\ln[-\ln(1-\alpha)] = \ln k + m \ln t \qquad (2)$$

where α, k and t are the extent of reaction, the rate constant and the firing time, respectively. The slope, m, determined by plotting the left-hand term in Equation 2 against $\ln t$, is a characteristic value for the mechanism of the rate process occurring in solid state reactions, that is, 0.5 for diffusion-controlled reactions [14–19], 2 or 3 for nucleation and growth of the product [10–13], and 1.1 for interfaces or phase boundary-controlled reactions [20].

Hulbert [21] has also stressed that in a nucleation-controlled reaction the value of the slope m will vary from 1.5 to 4 depending on the mechanism of the nucleation reaction, the nucleation rate, and the geometry of the nuclei, under the assumption that one reactant would be completely and constantly covered with the other reactant in the additive type of reaction.

Fig. 3 shows the relationship between $\ln\{\ln[1/(1-\alpha)]\}$ and $\ln t$. The results exhibit the presence of a main process which gives straight lines with slopes of 1.5 to 4 followed by a process with a slope of 0.5. In Sample III a process with a slope of 0.5 precedes the main process. The main processes with slopes of 1.5 to 4 would belong to the nucleation-controlled reaction [9, 21]. The subsequent process with a slope of 0.5 would be a diffusion-controlled reaction [9]. The formation of $ZnAl_2O_4$ apparently seems to cease after

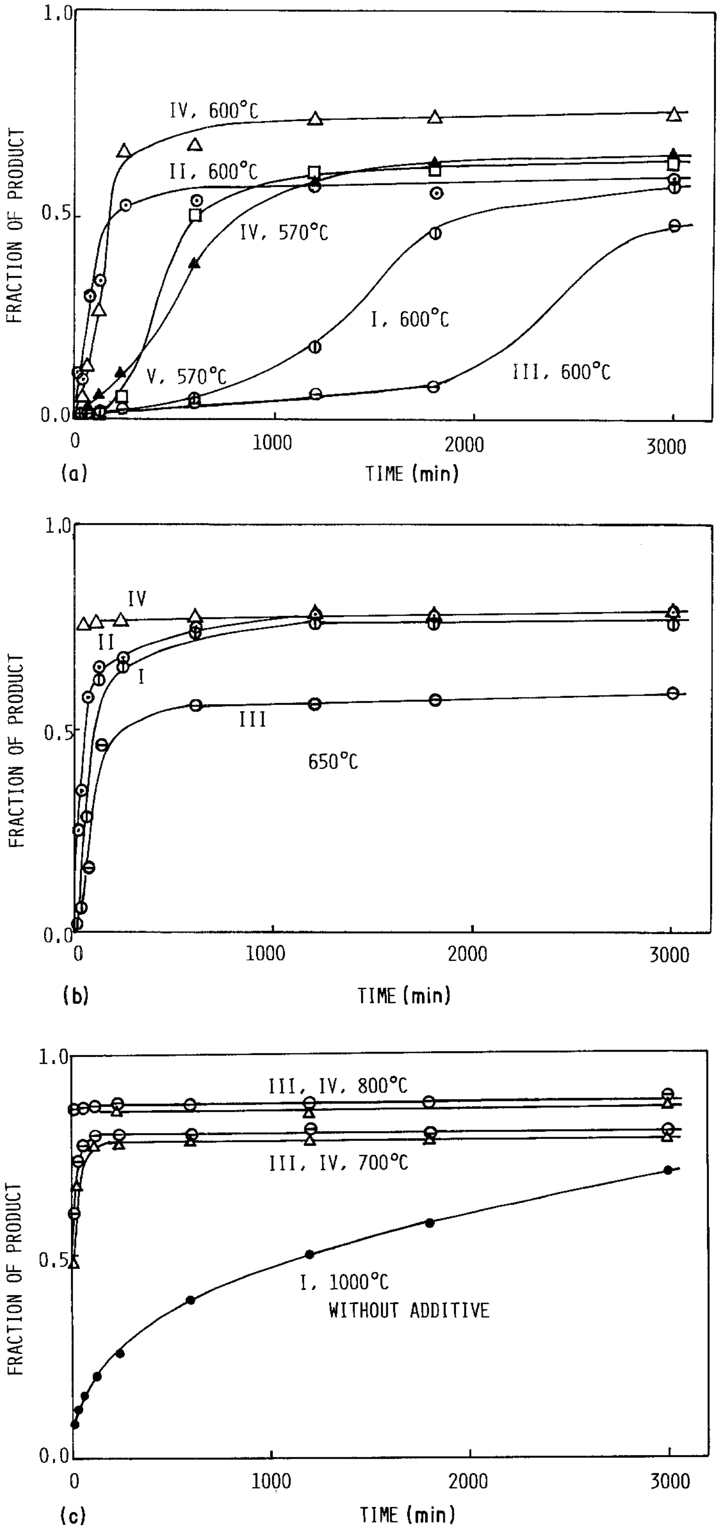

Figure 2 Rate curves of $ZnAl_2O_4$ formation in Samples I to V (see text) when fired at (a) 570 and 600° C, (b) 650° C and (c) 700 and 800° C.

the main nucleation period. When the process with a slope of 0.5 precedes the main process, it would be a diffusion-controlled dissolution process of ZnO and Al_2O_3 into the LiF phase to form an intermediate phase. This intermediate phase spreads out over the whole of the sample and the rapid formation of $ZnAl_2O_4$ by a nucleation-controlled process is initiated. The apparent cessation of $ZnAl_2O_4$ growth is due to the very low migration of reactants by diffusion through the $ZnAl_2O_4$ layer.

3.3. Temperature dependence of $ZnAl_2O_4$ formation rate

The rates of $ZnAl_2O_4$ formation at various temperatures were compared with different starting mixtures for various sources of Al_2O_3.

Fig. 4 shows the extent of reaction, α, after firing for 10 h at various firing temperatures, T. The formation of $ZnAl_2O_4$ in the presence of LiF starts at nearly 600° C. On the other hand, in additive-free samples $ZnAl_2O_4$ formation starts at 900° C. The additions of LiF lowered the starting temperature of $ZnAl_2O_4$ formation by about 300° C. The difference of the effect of the state of Al_2O_3 on $ZnAl_2O_4$ formation in the presence of LiF is remarkable for the initiation temperature. At higher firing temperatures such differences are not observable. The induction time before the start of rapid $ZnAl_2O_4$ formation depended on the source

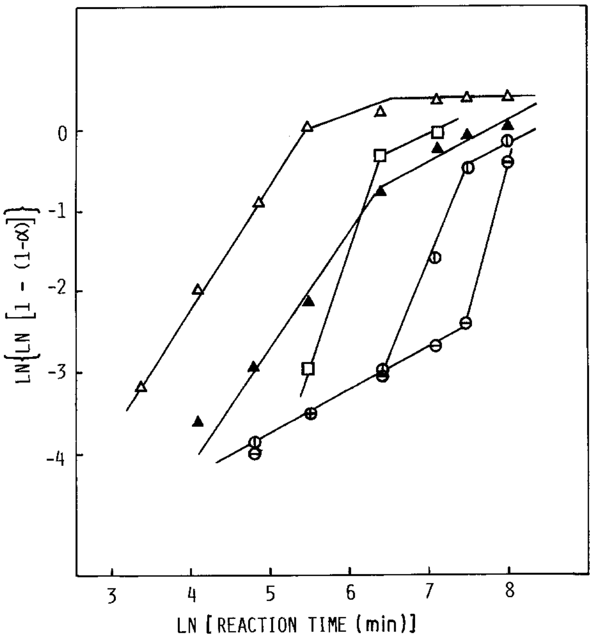

Figure 3 Analysis of the rate curves at low temperatures treated by the Hancock and Sharp method. (⦶) Sample I, 600° C; (⊖) Sample III, 600° C; (▲) Sample IV, 570° C; (△) Sample IV, 600° C; (□) Sample V, 570° C.

of Al_2O_3: Alumina A (small hard aggregates with adjusted particle size) < Alumina C (dense particle without agglomeration) < Alumina D (soft agglomerates of fine particles) < (A + B) and B (large hard aggregates). These results indicate that the dispersion and the packing state of the powders are important for the formation of an intermediate phase at the early stage of $ZnAl_2O_4$ formation in the presence of LiF, and are not any more effective for rapid $ZnAl_2O_4$ formation by a nucleation-limited process. Thus, the final extent of $ZnAl_2O_4$ formation has a same value, regardless of the state of Al_2O_3.

3.4. Effect of compaction pressure

The powder compact must be affected by the compaction pressure which affects the packing state (density of powder compact) and the contact state of the reactants. For this result, the extent of reaction will be influenced by the compaction pressure. Fig. 5 shows the change of the extent of the reaction by compaction pressure. The extent of the reaction is greatly dependent on the compaction pressure at the starting temperature of $ZnAl_2O_4$ formation, as seen in Fig. 5a. However, on elevating the firing temperature the effect of compaction pressure on the reactions disappeared and the extent of the reaction gave a constant value. On the other hand, in the absence of LiF no effect of compaction pressure was observed for $ZnAl_2O_4$ formation (Fig. 5b). In this case ZnO gas was transported directly to the reaction sites of $ZnAl_2O_4$ formation [1, 22, 23], i.e. the influence of packing state and inhomogeneity in the specimen can be eliminated from consideration. $ZnAl_2O_4$ formation in the presence of LiF at the initial stage was affected greatly by the compacting pressure.

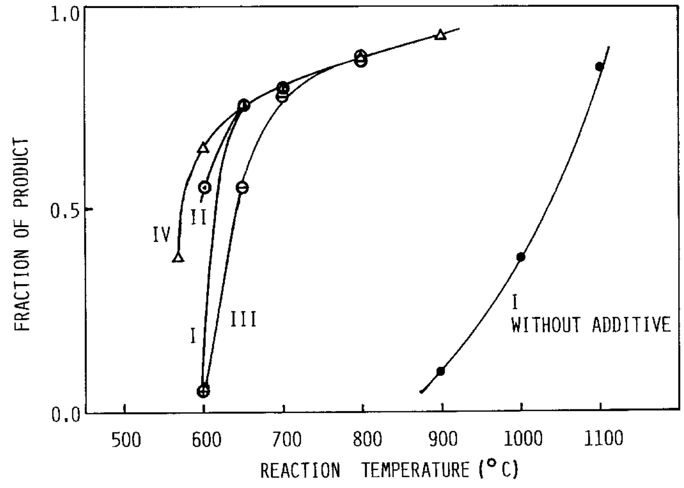

Figure 4 Extent of $ZnAl_2O_4$ formation in Samples I to IV when fired for 10 h at various temperatures.

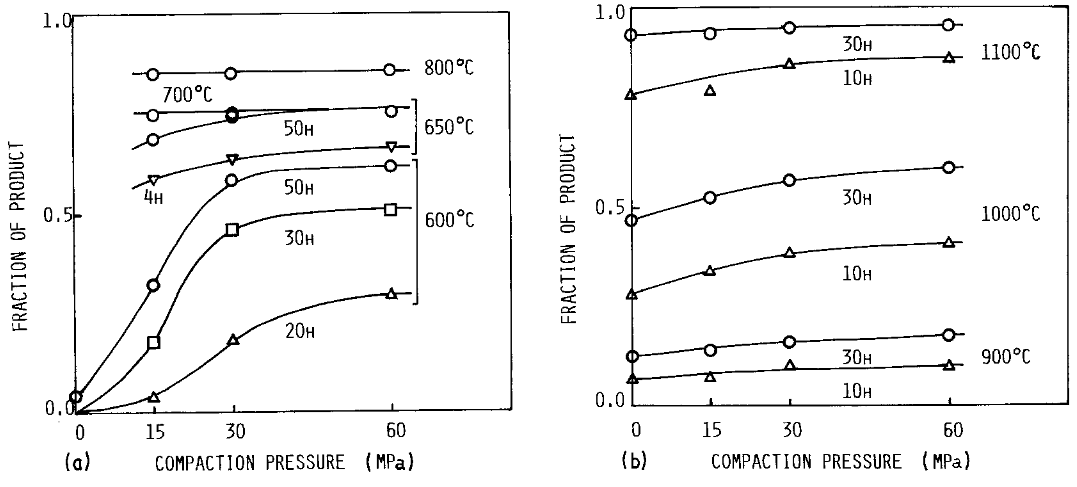

Figure 5 Effect of compaction pressure on $ZnAl_2O_4$ formation (a) with LiF and (b) without additives.

The large effect of compaction pressure on the initial stage of reaction, where an intermediate liquid phase is formed, indicates the importance of the contact between reactant particles.

4. Conclusions

It is concluded that the formation of $ZnAl_2O_4$ in the presence of LiF was significantly affected by the raw materials of alumina, and by the compaction pressure at the starting temperature. A typical sigmoid form was obtained in the rate curves. It was found that the main process is controlled by nucleation which is followed by a diffusion-controlled process. The amount of $ZnAl_2O_4$ decreased with an increase in the degree of agglomeration or aggregation when the firing temperature was at around 600° C, but no effect was observed at higher temperatures. Similar effects were also observed for the compaction pressures. These effects are interpreted as the results of the degree of the formation of a liquid intermediate phase.

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