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# Promotion of $ZnAl_2O_4$ formation by LiF

## Part 2 *Effect of particle size of alumina on the kinetics and microstructure of $ZnAl_2O_4$ formation in the presence of LiF*

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The effects of the particle size of $Al_2O_3$ on the formation of $ZnAl_2O_4$ in the presence of LiF were investigated. The promotion of $ZnAl_2O_4$ formation depended on the dissolution rate of $Al_2O_3$ into an intermediate phase which contained LiF, ZnO and $Al_2O_3$, i.e. the dissolution of $Al_2O_3$ was a key step for the promotion of the reaction. In order to promote the reaction it was necessary that the intermediate phase containing $Al_2O_3$ spread over the whole of the specimen before a dense $ZnAl_2O_4$ layer started to grow around the $Al_2O_3$ particles. Rapid dissolution of $Al_2O_3$ of a finer particle size than 10 $\mu$m was preferable for the promotion of $ZnAl_2O_4$ formation in the presence of LiF. Interference in $ZnAl_2O_4$ formation by the formation of a byproduct ($LiAl_5O_8$) was found in specimens containing a starting $Al_2O_3$ of grain size larger than 10 $\mu$m.

## 1. Introduction

In a powdered solid-state reaction, additions of additives are important to increase the amount of reaction products and to lower the initiation temperature of the reaction. The effectiveness of lithium fluoride is well known; for example, lithium fluoride has been used to produce transparent magnesia ceramics [1–3]. The physical nature of the raw materials significantly affects a powdered solid-state reaction. In a previous paper [4], the state of agglomeration and aggregation of alumina was studied with regard to its effect on the rate. The aim of this paper is to examine the effect of the particle size of $Al_2O_3$ on $ZnAl_2O_4$ formation in the presence of LiF. Measurements of the rate by chemical analysis and observation of the microstructures by a scanning electron microscope were performed.

## 2. Experimental procedure

### 2.1. Materials

Electrofused aluminium oxide of 98.5% purity from Fujimi Kenma Co., Nagoya 452, Japan, was used as the reactant source. Six kinds of alumina were prepared with particle sizes ranging over average diameters of 2, 5, 10, 23, 60 and 270 $\mu$m as measured by a scanning electron microscope (SEM). Fine zinc oxide powder was of the guaranteed reagent grade from Kishida Chemicals Co., Osaka 571, Japan. The particle size was measured by transmission electron microscopy (TEM) to be in the vicinity of 0.3 $\mu$m. Lithium fluoride was an extra-pure reagent from Nakarai Chemicals Co., Kyoto 604, Japan.

### 2.2. Sample preparation

Six reaction specimens containing 20 mol % of lithium fluoride were prepared by combining equimolar amounts of aluminium oxide of each different particle size with the fine zinc oxide. Six specimens were designated as Samples I to VI in the increasing order of particle size of alumina (see Section 2.1). Samples were mixed by shaking the powder in the dry state. The mixture was compacted under a pressure of 15 MPa. The compacts were fired in an electric furnace at 570 to 900° C for various durations up to 50 h.

### 2.3. Determination of the extent of $ZnAl_2O_4$ formation

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 Eriochrome Black T (EBT) as the indicator at pH 10.

### 2.4. Phase analysis and microstructural observation

Phases in the fired specimens were identified using conventional powder techniques of X-ray diffraction (XRD) analysis (Jeol Model JDX 7E). Green and fired compacts were impregnated in epoxy resin and subjected to grinding and final polishing with 2 $\mu$m diamond paste. Polished samples were observed by an optical microscope in reflected light and also by the SEM. The chemical composition of phases in the microstructure was analysed by an energy-dispersive X-ray microanalyser (EDX) (Horiba Ltd Model EMAX 8000 S) attached to the SEM. A Hitachi Model H 800 transmission electron microscope was also employed to determine the particle size of the starting powders.

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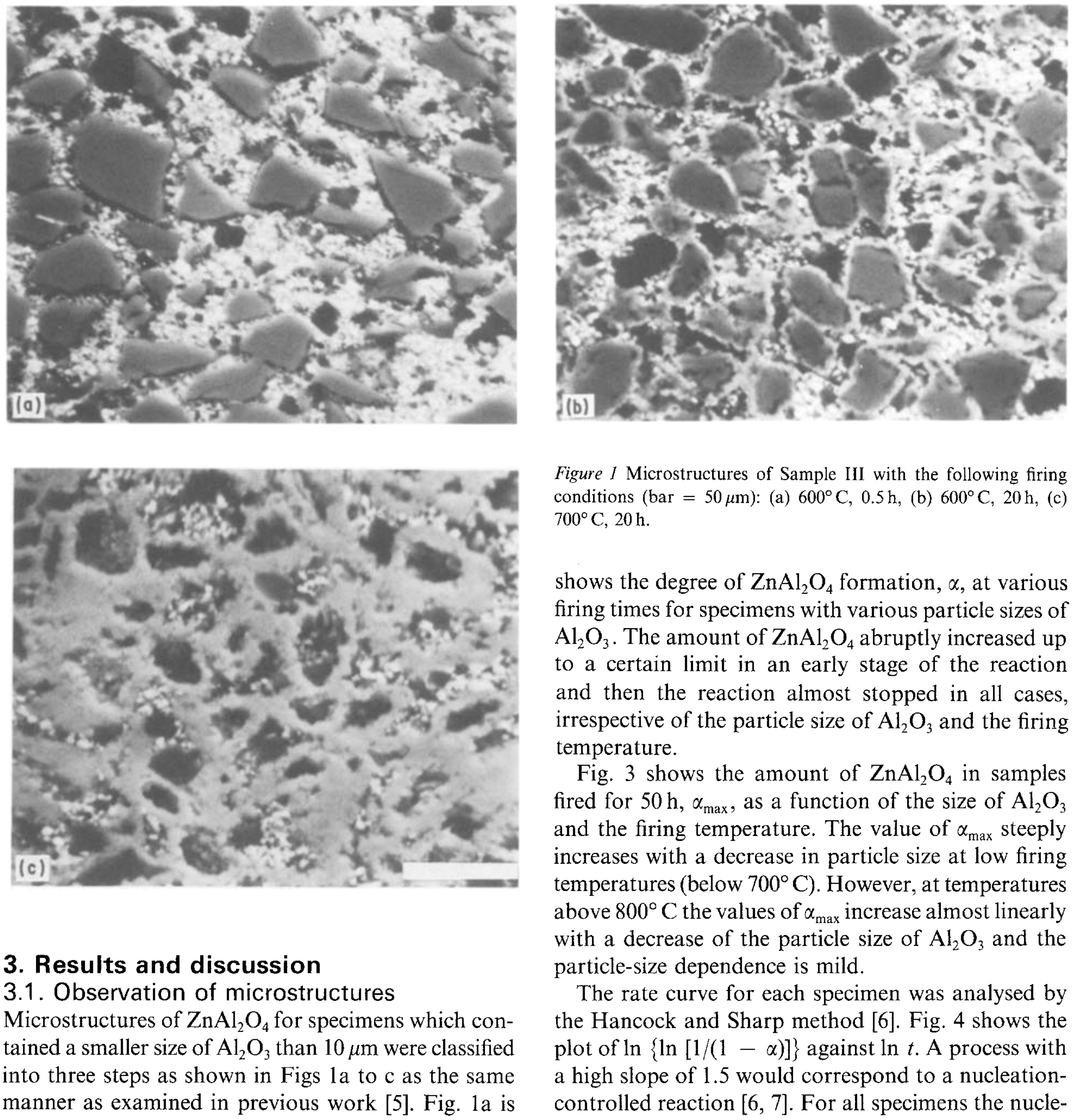

*Figure 1* Microstructures of Sample III with the following firing conditions (bar = $50\,\mu m$): (a) 600° C, 0.5 h, (b) 600° C, 20 h, (c) 700° C, 20 h.

## 3. Results and discussion

### 3.1. Observation of microstructures

Microstructures of $ZnAl_2O_4$ for specimens which contained a smaller size of $Al_2O_3$ than $10\,\mu m$ were classified into three steps as shown in Figs 1a to c as the same manner as examined in previous work [5]. Fig. 1a is the first step in the formation of an intermediate liquid phase by the corrosion of $Al_2O_3$ particles by fluoride liquid in the early stage of reaction, designated as Step I. The greyish particles are $Al_2O_3$. Zinc oxide surrounds the $Al_2O_3$ particles which have been corroded with fluoride liquid. Darkish particles of LiF can also be seen in the ZnO powder. In Step II, which is the middle stage, a $ZnAl_2O_4$ layer forms around the $Al_2O_3$ particles. A part of the intermediate liquid phase is present in the interspace between the $ZnAl_2O_4$ layer and the $Al_2O_3$ particle as shown in Fig. 1b. Step III, shown in Fig. 1c, represents the disappearance of $Al_2O_3$ particles in the final stage of the reaction. On the other hand, the specimens containing $Al_2O_3$ of a size larger than $10\,\mu m$ showed $ZnAl_2O_4$ formation with the formation of $LiAl_5O_8$, as shown in a previous paper [5].

### 3.2. Effect of particle size of alumina on the rate of $ZnAl_2O_4$ formation

The effects of the particle size of alumina on $ZnAl_2O_4$ formation in the presence of LiF were examined. Fig. 2 shows the degree of $ZnAl_2O_4$ formation, $\alpha$, at various firing times for specimens with various particle sizes of $Al_2O_3$. The amount of $ZnAl_2O_4$ abruptly increased up to a certain limit in an early stage of the reaction and then the reaction almost stopped in all cases, irrespective of the particle size of $Al_2O_3$ and the firing temperature.

Fig. 3 shows the amount of $ZnAl_2O_4$ in samples fired for 50 h, $\alpha_{max}$, as a function of the size of $Al_2O_3$ and the firing temperature. The value of $\alpha_{max}$ steeply increases with a decrease in particle size at low firing temperatures (below 700° C). However, at temperatures above 800° C the values of $\alpha_{max}$ increase almost linearly with a decrease of the particle size of $Al_2O_3$ and the particle-size dependence is mild.

The rate curve for each specimen was analysed by the Hancock and Sharp method [6]. Fig. 4 shows the plot of $\ln\{\ln[1/(1-\alpha)]\}$ against $\ln t$. A process with a high slope of 1.5 would correspond to a nucleation-controlled reaction [6, 7]. For all specimens the nucleation process has limited the initial stage of $ZnAl_2O_4$ formation, and the nucleation process was followed by a process with a low slope of 0.5 which corresponded to a diffusion-controlled reaction [6, 7]. For the specimens which contain larger sizes of $Al_2O_3$ than $10\,\mu m$, $ZnAl_2O_4$ formation has stopped, probably due to the appearance of $LiAl_5O_8$. For the specimens which contain smaller sizes of $Al_2O_3$ than $10\,\mu m$, $ZnAl_2O_4$ has been formed without the formation of $LiAl_5O_8$. Thus, the characteristic feature of the reaction in the variation of the particle size of $Al_2O_3$ is the appearance of $LiAl_5O_8$ above a certain size of alumina powder, and this inhibits the transport of material. The induction time at low firing temperatures could be avoided by decreasing the size of $Al_2O_3$ below $10\,\mu m$. These two factors would be helpful for the improvement of $ZnAl_2O_4$ formation by LiF. The rate curve for Sample I shows a brief induction time for $ZnAl_2O_4$ formation. The length, however, is insignificant compared with that for the specimen containing agglomerated $Al_2O_3$.

In the previous paper [4] it was revealed that inhomogeneities in the mixed state by uneven mixing,

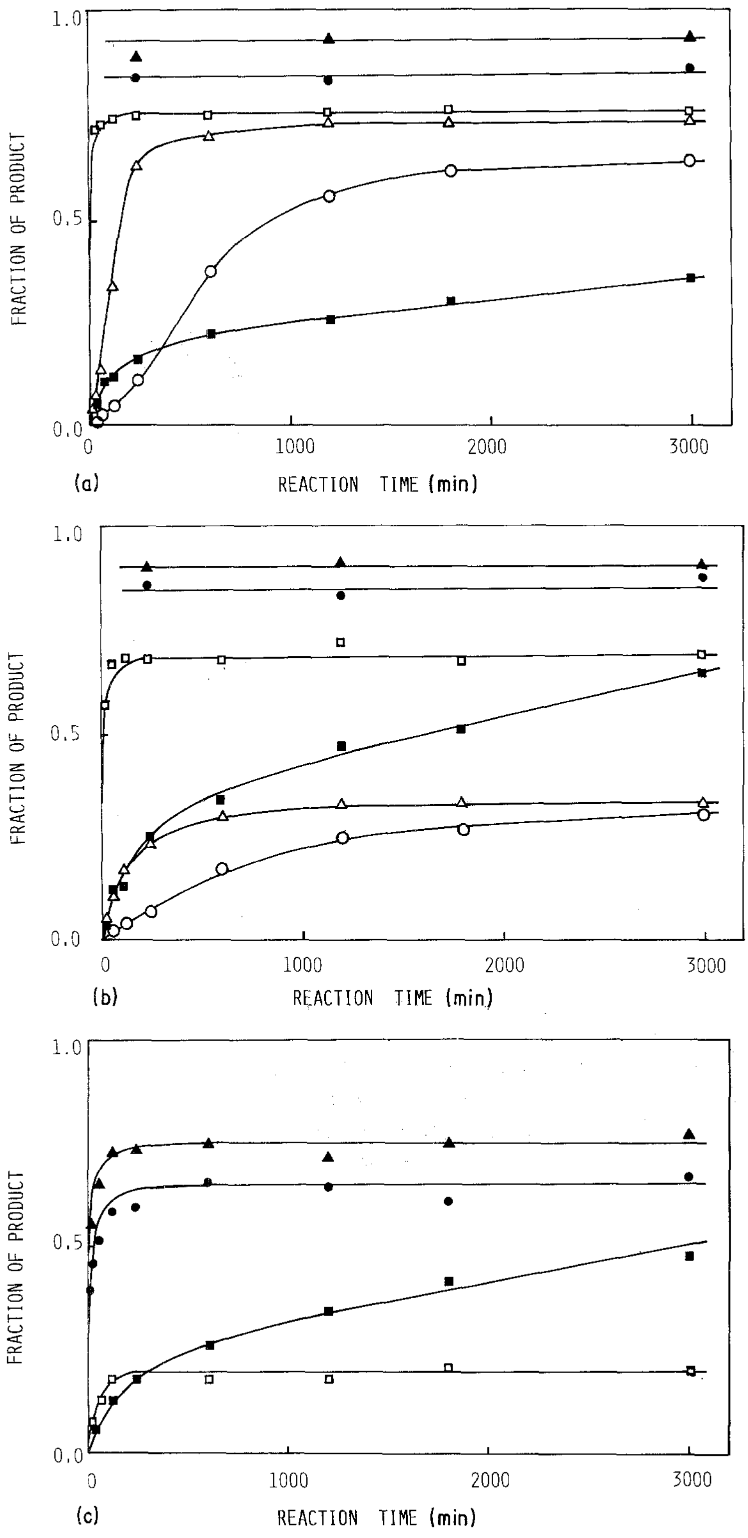

*Figure 2* Rate curves of $ZnAl_2O_4$ formation in (a) Sample I, (b) Sample III and (c) Sample V fired at various temperatures as a function of firing time. (○) 570° C, (△) 600° C, (□) 700° C, (●) 800° C, (▲) 900° C; (■) without additive at (a) 800° C, (b) 1000° C, (c) 1100° C.

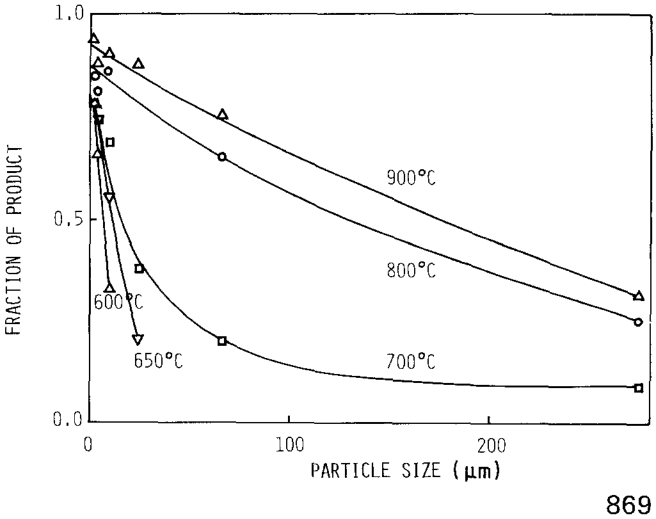

*Figure 3* Extent of $ZnAl_2O_4$ formation in Samples I to VI fired for 50 h at various temperatures as a function of the particle size of $Al_2O_3$.

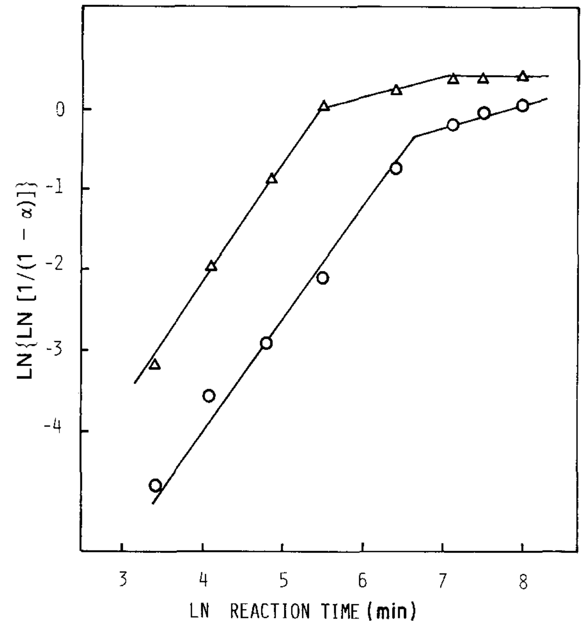

*Figure 4* Analysis of $ZnAl_2O_4$ formation in Sample I at low temperatures, treated by the Hancock and Sharp method. (○) 570° C, (△) 600° C.

and the formation of agglomerates and aggregates, resulted in an induction time. But in the examined range of the size of $Al_2O_3$ between 2 and 10 μm the length of the induction time was insignificant. The appearance of an induction time before $ZnAl_2O_4$ formation can be avoided by the use of $Al_2O_3$ in smaller particle sizes than 10 μm with no agglomeration and no aggregation.

## 3.3. XRD analysis of phases developed during the reaction

X-ray diffraction analysis was applied to examine the crystalline phases which appeared in the process of reaction during $ZnAl_2O_4$ formation in the presence of LiF with various particle sizes of $Al_2O_3$.

Fig. 5 shows the observed range of $ZnAl_2O_4$ formation, with or without $LiAl_5O_8$ formation, as a function of the size of $Al_2O_3$ and the firing temperature.

Lithium aluminate can be found in the ranges of larger $Al_2O_3$ particle sizes than 10 μm and higher firing temperatures than 700° C. As previously described [5], in the specimens prepared with a large size of $Al_2O_3$ a part of the intermediate liquid phase was confined in the interspace between the dense $ZnAl_2O_4$ layer and the $Al_2O_3$ particle. The dense $ZnAl_2O_4$ layer interfered with the spreading of liquid over the ZnO phase. $LiAl_5O_8$ has also deposited on the $ZnAl_2O_4$ layer from the confined liquid.

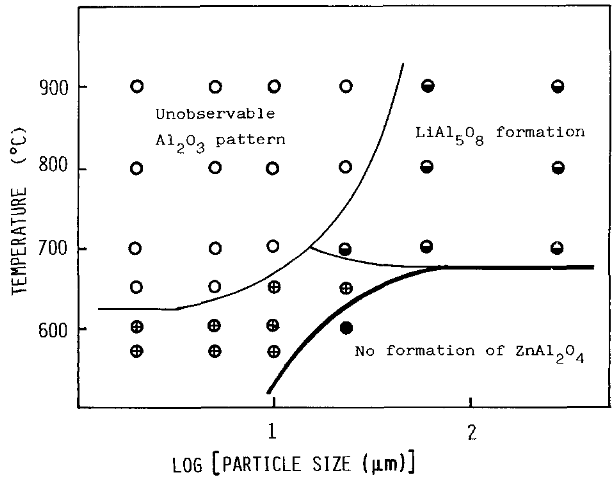

*Figure 5* Observed range of each phase detected by X-ray diffraction analysis as a function of firing temperature and the particle size of $Al_2O_3$.

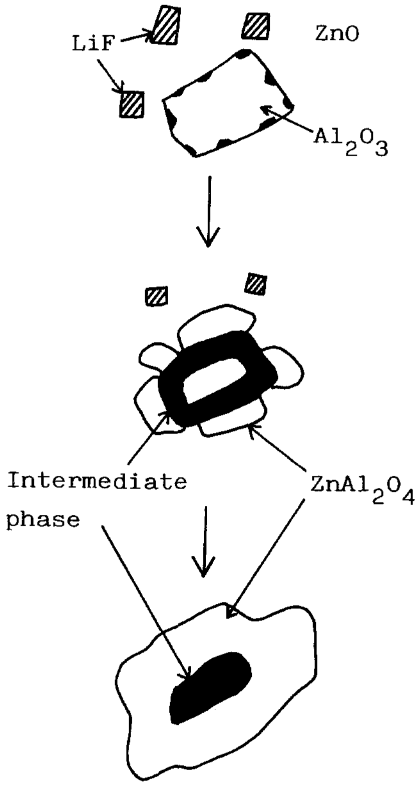

*Figure 6* Schematic reaction model for a specimen with fine $Al_2O_3$.

On the other hand, the $Al_2O_3$ phase has completely dissolved without forming $LiAl_5O_8$ in Samples I to III with fine $Al_2O_3$ particle sizes under 10 μm and an elevation of firing temperature to higher than 700° C. Fig. 6 shows a schematic reaction model for specimens prepared with a small size of alumina. As seen in Fig. 6, fast spreading of alumina over the whole of the specimen is possible by rapid and complete dissolution of $Al_2O_3$ into the liquid before the formation of a dense $ZnAl_2O_4$ barrier inhibits the intermediate liquid phase from spreading and induces $LiAl_5O_8$ to crystallize.

## 4. Conclusions

It is concluded that the formation of $ZnAl_2O_4$ in the presence of LiF was remarkably affected by the particle size of $Al_2O_3$ starting material. Interference in $ZnAl_2O_4$ formation by the formation of a by-product ($LiAl_5O_8$) was found in specimens containing starting $Al_2O_3$ of grain sizes larger than 10 μm. Promotion of $ZnAl_2O_4$ formation was dependent on the dissolution rate of $Al_2O_3$ into the intermediate phase, which was a key step in the promotion of the reaction. It was necessary that the intermediate phase containing $Al_2O_3$ spread over the whole of the specimen before the growth of a dense $ZnAl_2O_4$ barrier around the $Al_2O_3$ particle. In order to promote $ZnAl_2O_4$ formation, the use of $Al_2O_3$ finer than 10 μm was preferable in the presence of LiF to avoid the formation of $LiAl_5O_8$.

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