Effects of Additives on Solid State Reaction. I. A Kinetic Study of the Effects of Halides of the Formation of $MgAl_2O_4$

Shiro Shimada, Ryusaburo Furuichi, and Tadao Ishii
Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060

(Received July 9, 1973)

The mechanism for the promoting effects of additives on the formation of $MgAl_2O_4$ has been systematically discussed from the results of kinetic measurements. A mixture of MgO and α-Al_2O_3 powder containing 10 mol% additives (LiF, NaF, MgF_2, CaF_2, BaF_2, NaCl or $CaCl_2$) and that without additives were isothermally heated in N_2 atmosphere in the temperature ranges 670—1142 °C and 1190—1360 °C. The diffusion-controlled Jander's equation was applied to all kinetic data obtained. In the case of fluoride additives, it has been found that the promoting actions are in the order $LiF \geq NaF > BaF_2 > MgF_2 > CaF_2$ and that the cations of fluorides play an important role in accelerating diffusion. The same promoting mechanism seems to be applicable in the case of chloride additives.

Solid state reactions are affected by various factors such as impurities or additives, preparation history of reacting material and atmosphere.[1,2] The effect of additives on the solid state reaction in MgO–Al_2O_3 system has been investigated by several authors.[3–5] Little attention, however, has been paid to the effect of additives on the solid state reaction, no explanation being given on their actions from a kinetic viewpoint.

In this paper, the promoting actions of alkali and alkaline earth halides on the formation of $MgAl_2O_4$ were discussed on the basis of the kinetic data. It was examined whether a mechanism similar to that for $MgCl_2$[6] additive could be applied to other chlorides.

Experimental

Sample. α-Al_2O_3 samples were prepared by calcining active alumina (Merck Co., 99.9% pure) at 1300 °C for 2 hr in the air. MgO samples were prepared from $Mg(OH)_2$ (Kanto Chemical Co., G.R. grade) under the same conditions. The particle size of α-Al_2O_3 was microscopically estimated to be in the range 58—90 μ, with an average of 70 μ. The MgO was found to have an average particle size of 0.1 μ by electron-microscopic observation. Powders of MgO, α-Al_2O_3 and additive were well mixed in the molar ratio 1 : 1 : 0.1. The additives used were LiF, NaF, MgF_2, CaF_2, BaF_2, NaCl and $CaCl_2 \cdot H_2O$ and were stored in a desiccator with silica gel before experiments. The additives (Kanto, Wako or Morita Companies) were of G.R. grade. The mixtures were pressed into pellets at 150 kg/cm^2 except for $CaCl_2 \cdot H_2O$ additive. The powders of MgO, α-Al_2O_3 and $CaCl_2 \cdot H_2O$ were mixed in a dry box because of the hygroscopic nature of $CaCl_2 \cdot H_2O$. These powder mixtures were heated at 400 °C to dehydrate $CaCl_2 \cdot H_2O$ prior to the kinetic experiment.

Kinetic Measurements. Two furnaces, Pt- and SiC-electric furnaces, were used for the measurements. The Pt-furnace was used for MgO–Al_2O_3–additive (LiF, NaF, MgF_2, BaF_2, NaCl or $CaCl_2$) systems in the temperature range 670—1100 °C). The furnace was equipped with a fused-silica tube connected to the vacuum system in which static nitrogen pressure was kept at 300 mmHg. The SiC-furnace was used for MgO–Al_2O_3 and MgO–Al_2O_3–CaF_2 systems in the temperature range 1100—1360 °C. This was equipped with a mullite tube through which nitrogen was allowed to flow at a rate of 30 ml/min. Compact pellets were placed on a Pt-boat in the tube and then heated isothermally. The temperature was measured with a Pt-Pt13Rh thermocouple.

Conversion of $MgAl_2O_4$ was determined by measuring the amount of the remaining MgO or α-Al_2O_3 after the reaction. The MgO unreacted was dissolved in 1.0 M nitric acid. The procedure was applied to the samples in the experiments of MgO–Al_2O_3 system and MgO–Al_2O_3–additive (LiF, NaF, NaCl or $CaCl_2$) system. Before titration, $CaCl_2$ was removed by washing the sample with alcohol. The amount of unreacted α-Al_2O_3 was estimated from the quantitative X-ray analysis by using CaF_2 as an external standard. This method was applied to the samples obtained from the MgO–Al_2O_3–additive (MgF_2, CaF_2 or BaF_2) systems. The results are shown in Table 1, and a satisfactory agreement can be seen between the chemical analysis and X-ray method.

Table 1. Fractional conversion (%) of $MgAl_2O_4$ for MgO–Al_2O_3 system

Chemical analysis	X-Ray analysis
$\alpha = 23$	$\alpha = 24$
26	30
36	37
42	45
46	48
94[a]	93[a]

a) results for 10 mol % additive of NaF

Reaction in MgO–Al_2O_3–additive System by the use of Pellets of MgO and α-Al_2O_3 (Model experiments). MgO and α-Al_2O_3 pellets, *ca.* 1 mm thick, were obtained by heating the compressed powders of MgO and α-Al_2O_3 at 1300 °C for 3 hr in the air. The experiment was carried out in the temperature range 900—950 °C for 5 hr in a vacuum (10^{-1} mmHg). The samples were prepared by sandwiching the powders of additives *ca.* 0.1 mm thick (LiF, NaF, BaF_2, LiCl, NaCl or $CaCl_2$) between MgO and α-Al_2O_3 pellets. After the reaction, the chlorides adhering to the pellets were removed by washing with alcohol in order to observe the surfaces and to measure the weight change of the pellets.

DTA Experiments. DTA experiments on the MgO–Al_2O_3–NaF system were carried out in nitrogen atmosphere at a heating rate of 10 °C/min. The sample was a mixture of MgO, α-Al_2O_3 and NaF with mol ratio 1 : 1 : 0.1, its weight being 300 mg.

Results and Discussion

Formation Rate of $MgAl_2O_4$. The rate of reaction between reactant particles is generally governed by either phase-boundary process or diffusion process.[7] The equations for the diffusion-controlled reaction have been given by Jander,[8] Serin-Ellickson,[9] Ginstling-Brounshtein,[10] and Carter.[11] Jander's equation is

$$[1-(1-\alpha)^{1/3}]^2 = kt \qquad (1)$$

$$k = 2DC_0/R^2 \qquad (2)$$

where α=fractional conversion, k=rate constant, t=reaction time, D=diffusion coefficient, C_0=concentration of reactant at the interface, and R=particle radius.

The formation rates of $MgAl_2O_4$ in MgO–Al_2O_3 system and MgO–Al_2O_3–additive systems are shown in Figs. 1 and 2. All the data were obtained from the pellet except for the $CaCl_2$ additive (Fig. 2-D). The ⊗ marks in Fig. 1-A indicate the α values for loosely packed powder mixtures of MgO and α-Al_2O_3 heated at 1190 °C. Little difference was observed in the α values between the loosely packed powders and the compacted pellets under these experimental conditions.

A part of the data given in Figs. 1 and 2 plotted according to Eq. (1) is shown in Fig. 3. It can be seen that the data can fit Jander's equation up to about α=70%. For MgO–Al_2O_3 mixtures (Fig. 3-B, ○ and ●) and those containing the fluoride additives (Fig. 3-A), the straight lines intersect the ordinate at kt values corresponding to α=20—30%. The fluoride additives seem to show larger intersecting values than those for non-additives systems. The straight lines of the chloride additives, however, fall approximately on the original point (Fig. 3-B). It seems that in the case of the fluoride additives, the initial formation of $MgAl_2O_4$ results from the reaction at the surface between the particles, and the subsequent reaction proceeds by the diffusion of the reactants through the $MgAl_2O_4$ layer formed. Abrupt change in slope was observed only for LiF additive system (Fig. 3—A, ○ and ●).

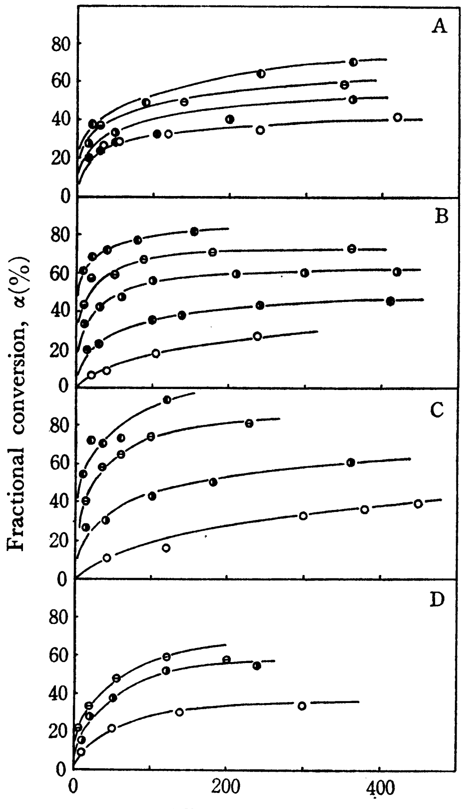

Fig. 1. Formation rate of $MgAl_2O_4$ for the MgO–Al_2O_3 and the MgO–Al_2O_3–alkali halide systems.
A : MgO–Al_2O_3 system
○: 1190 °C, ◑: 1240 °C, ⊖: 1295 °C,
◐: 1357 °C, ⊗: 1190 °C, results from the loosely packed powders
B : MgO–Al_2O_3–LiF system
○: 670 °C, ⊗: 714 °C, ◑: 753 °C, ⊖: 800 °C
◐: 850 °C
C : MgO–Al_3O_3–NaF system
○: 757 °C, ◑: 800 °C, ⊖: 840 °C, ◐: 870 °C
D : MgO–Al_2O_3–NaCl system
○: 965 °C, ◑: 1006 °C, ⊖: 1040 °C

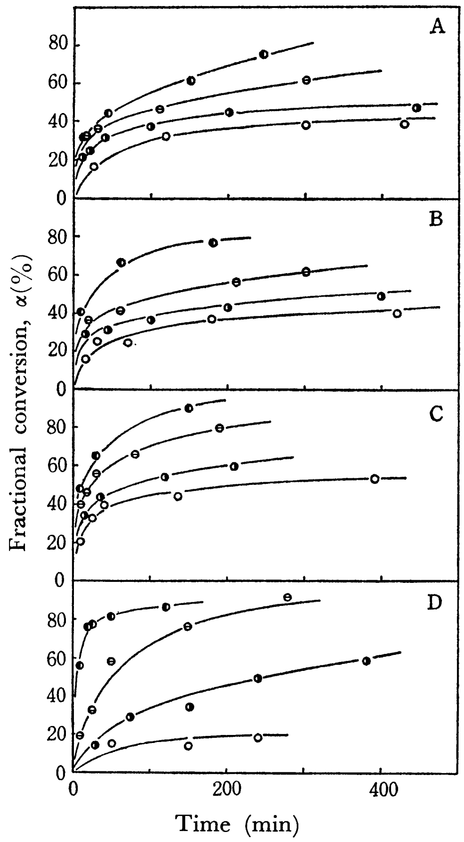

Fig. 2. Formation rate of $MgAl_2O_4$ for the MgO–Al_2O_3–alkaline earth halide system.
A : MgO–Al_2O_3–MgF_2 system
○: 985 °C, ◑: 1025 °C, ⊖: 1070 °C,
◐: 1100 °C
B : MgO–Al_2O_3–CaF_2 system
○: 1025 °C, ◑: 1056 °C, ⊖: 1100 °C,
◐: 1142 °C
C : MgO–Al_2O_3–BaF_2 system
○: 865 °C, ◐: 915 °C, ⊖: 960 °C, ◐: 990 °C
D : MgO–Al_2O_3–$CaCl_2$ system, the loosely packed powder samples
○: 860 °C, ◑: 900 °C, ⊖: 953 °C, ◐: 1003 °C

The rate constant k can be estimated from the slope of line in Fig. 3. The activation thermodynamic functions, ΔG^*, ΔH^*, ΔS^*, are calculated by

$$k = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \qquad (3)$$

where R=gas constant, T=absolute temperature, N=Avogadro's number, and h=Planck's constant. The transmission coefficient is assumed to be unity. The

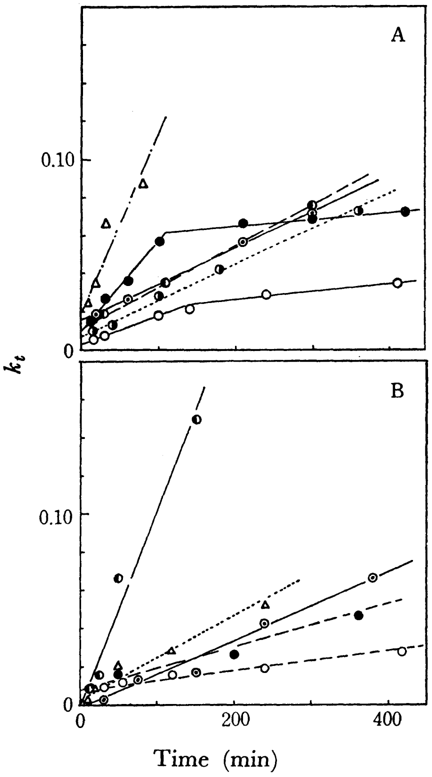

Fig. 3. Plots of k_t *vs.* t according to the Jander's equation.

A: ○: 714 °C } LiF
●: 753 °C
◑: 800 °C } NaF
◐: 1070 °C } MgF_2
⊙: 1100 °C } CaF_2
△: 960 °C } BaF_2

B: ○: 1190 °C } non-additive
●: 1240 °C
△: 1006 °C } NaCl
⊙: 900 °C } $CaCl_2$
◐: 953 °C

values listed in Table 2 illustrate how greatly the formation reaction of $MgAl_2O_4$ is promoted by the presence of the additives. From the values for $\varDelta G^*$, the promoting actions of the additives can be represented by the sequences, LiF ≥ NaF > BaF_2 > $CaCl_2$>NaCl>MgF_2>CaF_2.

A comparison of the activation thermodynamic functions for the various additive systems with those for the non-additive system also shows that the additive systems give the values of $\varDelta H^*$ and $\varDelta S^*$ differing from those for non-additive system. This suggests that the diffusion mechanism in the additive systems differs from that in the non-additive system.

Halvac[12] studied the reaction of the powder compacts of α-Al_2O_3 and MgO in the air, in the temperature range 1000—1290 °C, and suggested that the formation rate of $MgAl_2O_4$ was controlled by either grain-boundary or volume diffusion step. The values of D in this temperature range have been calculated to be $D=10^{-12}$ 10^{-10} cm^2/s in the temperature range 1190—1360 °C, by assuming that $R=0.007$ cm, $C_0=1.0$[13] in Eq. (2). The value closely agrees with Halvac's. For LiF, NaF, BaF_2 and $CaCl_2$ additives, the values of D were also found to be $D=10^{-10}-10^{-8}$ cm^2/s in the temperature range 800—1000 °C, which was larger than the value of D for the non-additive system by a factor of 10^3—10^5, when D's at 800—1000 °C were corrected for 1190—1360 °C. The comparable values of D for the non-additive system therefore show that the grain-boundary or volume diffusion should be operative in the formation of $MgAl_2O_4$. On the other hand, the significant increase in the value of D in the case of LiF, NaF, BaF_2 and $CaCl_2$ additives indicates that these additives exert an enhancing action on the diffusion along grain-boundary or within bulk.

Model Experiment. The formation of $MgAl_2O_4$ in the systems with fluoride additives seems to consist of two stages; rapid reaction at the surface between the particles in the initial stage and diffusion in the later stage. In order to examine the rapid reaction at the surface, model experiments were carried out by using α-Al_2O_3 and MgO pellets between which the fluorides were placed.

Although the chloride additions showed no such rapid reaction at the surface, the interactions of chlorides with MgO or α-Al_2O_3 were examined by model experiments.

Fluoride: The model reaction on MgO–Al_2O_3–fluoride (LiF, NaF or BaF_2) systems was carried out at 950 °C for 5 hr in a vacuum.

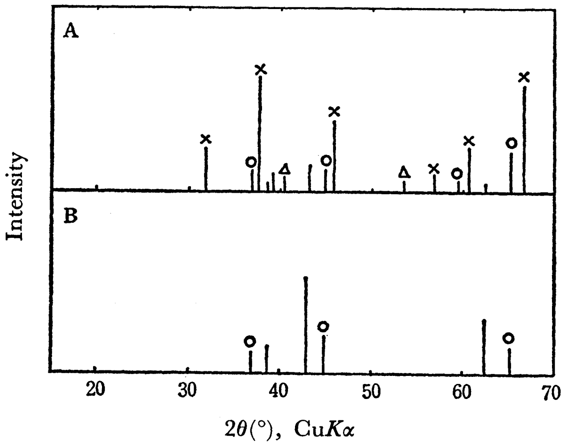

Fig. 4. X-ray diffraction patterns of the reaction surface of α-Al_2O_3 and MgO pellets in the MgO–Al_2O_3–LiF system.
Reaction temperature: 950 °C, time: 5 hr, in vacuum (10^{-1} mmHg).
A: α-Al_2O_3 pellet, B: MgO pellet
○: $MgAl_2O_4$, ×: $LiAl_5O_8$, △: MgF_2

Figure 4 shows the X-ray diffraction patterns of the surface of α-Al_2O_3 and MgO pellets obtained by the reaction in MgO–Al_2O_3–LiF system. We see that $LiAl_5O_8$ is formed on the surface of α-Al_2O_3 pellet (Fig. 4-A). Another two experiments showed that $NaAl_{11}O_{17}$ and $BaAl_2O_4$ were formed on the surface of α-Al_2O_3 pellet in the reaction of MgO–Al_2O_3–NaF system and MgO–Al_2O_3–BaF_2 system, respectively. $NaAl_{11}O_{17}$ was assumed to result from unreacted α-Al_2O_3 and $Na_2Al_2O_4$ formed from α-Al_2O_3 and NaF.[14] Thus, it can be concluded that the reaction of α-Al_2O_3 with fluoride results in the formation of aluminate.

Chloride: The model reactions of MgO–Al_2O_3–chloride ($CaCl_2$, LiCl or NaCl) systems were performed at 900—950 °C for 5 hr in a vacuum.

Table 2. Activation thermodynamic functions for formation reaction of $MgAl_2O_4$

Additive	React. temp. (°C)	k (min^{-1})	ΔG^* (kcal/mol)	ΔH^* (kcal/mol)	ΔS^* (cal/mol·deg)
non-additive	1190	3.80×10^{-5}	121	68	−36
	1240	8.50×10^{-5}	123		
	1295	1.48×10^{-4}	125		
	1357	2.75×10^{-4}	127		
LiF	670	4.00×10^{-5}	76	50	−28
	714	1.42×10^{-4}	78		
	753	4.70×10^{-4}	79		
	800	9.86×10^{-4}	80		
	850	1.60×10^{-3}	82		
NaF	757	5.17×10^{-5}	83	87	+3
	800	1.87×10^{-4}	83		
	840	1.37×10^{-3}	83		
	870	2.80×10^{-3}	83		
NaCl	965	3.97×10^{-5}	101	104	+3
	1006	1.77×10^{-4}	101		
	1040	4.65×10^{-4}	101		
MgF_2	985	3.50×10^{-5}	103	77	−21
	1025	8.50×10^{-5}	104		
	1070	2.13×10^{-4}	105		
	1100	4.87×10^{-4}	106		
CaF_2	1025	4.90×10^{-5}	105	67	−30
	1056	9.30×10^{-5}	106		
	1100	2.07×10^{-4}	108		
	1142	7.10×10^{-4}	109		
BaF_2	865	9.00×10^{-5}	91	60	−27
	915	2.50×10^{-4}	92		
	960	8.20×10^{-4}	94		
	990	2.00×10^{-3}	94		
$CaCl_2$	860	2.10×10^{-5}	92	113	+18
	900	1.82×10^{-4}	92		
	953	1.60×10^{-3}	91		
	1003	7.39×10^{-3}	90		

Table 3. Weight change of pellets of MgO and α-Al_2O_3 for the model reactions in the MgO-Al_2O_3-chloride systems

Additives	React. temp. (°C)	React. time (hr)	Melting point of additives[a] (°C)	Weight changes (mg)	
				MgO[b]	α-Al_2O_3[c]
$CaCl_2$	900	5.0	782	− 2	+ 5
$CaCl_2$	950	5.0	782	−21	+10
LiCl	940	5.0	610	− 4	+14
NaCl[d]	950	5.0	808	—	—
non-additive	960	5.0	—	0	0

a) From Ref. 15. b) weight loss of MgO pellets. c) Weight increase of α-Al_2O_3 pellets. Two pellets of MgO and α-Al_2O_3 could not be separated. The reacted surface of α-Al_2O_3 pellet obtained was exposed by polishing.

The weight changes of MgO and α-Al_2O_3 pellets and the melting point of additives are given in Table 3. The weight of MgO pellets is seen to decrease and that of α-Al_2O_3 pellets to increase. The X-ray diffraction patterns of the reacted surface of the pellets indicate that $MgAl_2O_4$ is formed only on the α-Al_2O_3 surface. These results suggest that molten chloride behaves as a vehicle, in which MgO is dissolved to disperse uniformly, and the molten phase containing MgO is transported into the α-Al_2O_3 particle which is an agglomerate of the crystallites.

Promoting Actions of Additives. *Fluoride*: From the results it seems that a large part of the cations of fluoride exists in the form of aluminate which is incorporated into $MgAl_2O_4$ layer. Thus, it is necessary to examine whether such cations exert an influence on the diffusion process.

The plots of log ($k_{additive}/k_{pure}$) for 1173 K against the electronegativity of cations[16)] are shown in Fig. 5. The logarithmic ratios corrected for $T=1174$ K were calculated by means of Eq. (3) and the value of the thermodynamic functions in Table 2. The figure shows an exponential increase in the formation rate with the decrease in the electronegativity of cations. The activation enthalpy, ΔH^*, can be correlated with the electronegativity as shown in Fig. 6; the value of ΔH^* decreases linearly with the decrease in the electronegativity except for the NaF additive. It can be concluded

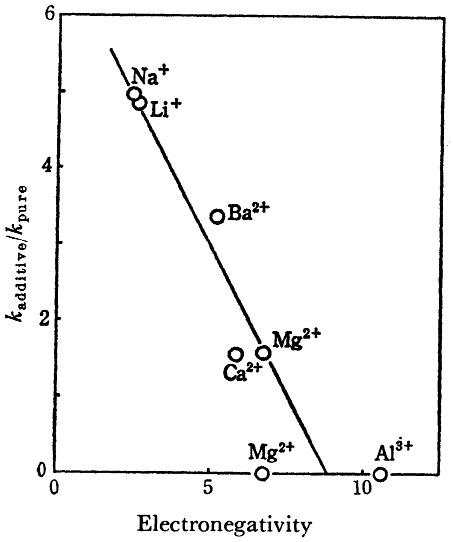

Fig. 5. Relationship between log ($k_{\text{additive}}/k_{\text{pure}}$) and the electronegativity of cations of fluorides.

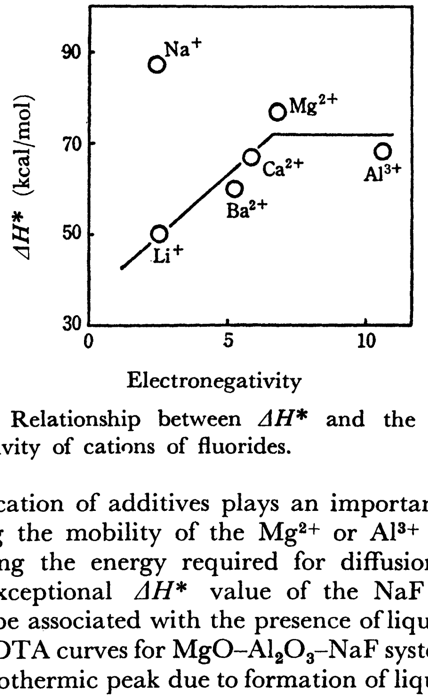

Fig. 6. Relationship between ΔH^* and the electronegativity of cations of fluorides.

that the cation of additives plays an important role in increasing the mobility of the Mg^{2+} or Al^{3+} ions and in lowering the energy required for diffusion.

The exceptional ΔH^* value of the NaF additive seems to be associated with the presence of liquid phase, since the DTA curves for $MgO-Al_2O_3-NaF$ system showed an endothermic peak due to formation of liquid phase at near 800 °C. A similar relation between the large ΔH^* and the presence of liquid phase holds for the cases of $CaCl_2$ ($\Delta H^*=113$ kcal/mol) and NaCl ($\Delta H^*=104$ kcal/mol) additives which are in liquid state at the reaction temperatures. The presence of liquid phase in the course of the reaction might be associated with the possitive value of ΔS^* of these additives (Table 2) which shows an activated state disordered more than the reactants.

Chloride: The same mechanism as that for the molten $MgCl_2$ may be applied to the other chloride additives since they are in liquid state at reaction temperatures. MgO particles may dissolve in the molten chloride, then they spread uniformly over the surface of α-Al_2O_3 particles and are transported to the inner part of α-Al_2O_3 particles consisting of the crystallites. In such cases, the value of C_0 in Eq. (2) is expected to be large and the diffusion distance reduced from the radius ($R=70\ \mu$) of α-Al_2O_3 particle to that ($R=1$—$2\ \mu$) of α-Al_2O_3 crystallites. However, such a reduction of distance would not occur in the non-additive system because of the absence of molten phase.

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