Effect of Additive on Solid State Reaction. II. A Thermoanalytical Study of the Effect of Fluorides on the Formation of $MgAl_2O_4$ in Initial Stage

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The promoting actions of fluoride on the formation of $MgAl_2O_4$ in the initial stage have been studied by means of DTA and high-temperature X-ray diffraction techniques. LiF, NaF, MgF_2, CaF_2 and BaF_2 were used as additives. The three MgO–Al_2O_3–fluoride (LiF, NaF or BaF_2) systems showed similar DTA curves; an endothermic peak (peak-1) in the temperature range 660—800 °C, followed by an exothermic peak (peak-2) at 700—900 °C. The DTA curves for MgO–Al_2O_3–fluoride (MgF_2 or CaF_2) systems showed no thermal change. It was found that peak 1 corresponds to Reaction (2), $3MF+2Al_2O_3=3MAlO_2+AlF_3$, and peak 2 to Reaction (1), $3MgO+2AlF_3=3MgF_2+Al_2O_3$, and the formation of $MgAl_2O_4$. It was concluded that Reaction (2) takes place before the formation of $MgAl_2O_4$ and that AlF_3 resulting from Reaction (2) initiates the formation of $MgAl_2O_4$.

In the preceding paper[1] the promoting actions of fluorides and chlorides on the formation of $MgAl_2O_4$ were discussed from a kinetic viewpoint. Rate constants were obtained from isothermal experiments for determining the extent of promoting action. Some clues for the reaction mechanism such as a linear relation between the rate constant and electronegativity of cations of the halides were also obtained. However, it was not possible to see what kind of chemical reaction between the halide additives and reactants MgO and Al_2O_3 promotes the formation. DTA and high-temperature X-ray diffraction, both being non-isothermal techniques, are useful for clarifying the reaction over a wide temperature range and for finding the initiation temperature of the reaction. We have studied MgO–Al_2O_3–fluoride systems by the non-isothermal technique in order to find the chemical reaction between additive and reactant.

Experimental

Sample. α-Al_2O_3 and MgO samples were prepared by a method similar to that described.[1] The particle size of sample was smaller than 44 μ for α-Al_2O_3 and *ca.* 0.1 μ for MgO. The fluorides used as additive were LiF, NaF, MgF_2, CaF_2 and BaF_2.

DTA Experiments. DTA experiments were carried out with a Thermoflex 8001 type apparatus (Rigaku-Denki). Before heating the sample, the apparatus was evacuated to approximately 10^{-1} mmHg and then filled with N_2 of 300 mmHg to avoid the effect of water vapor in the air. Pt-Pt13Rh thermocouples were used for measuring the temperature, a heating rate of 10 °C/min being employed in all experiments. The sample weight was about 300 mg. α-Al_2O_3 of the same weight was taken as the standard material.

X-Ray Diffraction. A Geigerflex 2141 type diffractometer (Rigaku-Denki) was used for X-ray analysis of the samples obtained during DTA runs, the analysis being carried out with Ni-filtered Cu$K\alpha$, operation voltage 25 kV and current 10 mA. The fractional conversion of $MgAl_2O_4$ was determined by the quantitative X-ray analysis.[1]

High-temperature X-Ray Diffraction. A high-temperature A-4 type attachment (Rigaku-Denki) was used. The experiments were carried out in static N_2 of 300 mmHg at heating rate of 2—4 °C/min, operation voltage and current respectively 40 kV and 20 mA.

Results and Discussion

MgO–Al_2O_3–LiF System. The change of high-temperature X-ray diffraction intensities with the reaction temperature is shown in Fig. 1. Curve a: (113) line of α-Al_2O_3, Curve b: (200) of MgO, Curve c: (400) of $MgAl_2O_4$, Curve d: (200) of LiF. We see that $MgAl_2O_4$ begins to form simultaneously with the decrease of the reactants of MgO, α-Al_2O_3 and LiF near 630 °C, and that in the initial stage of the $MgAl_2O_4$ formation, the extent of the decrease in the X-ray intensity with temperature is larger for α-Al_2O_3 than for MgO. The shift of (200) diffraction line of LiF to the lower angle starts at a temperature near 400 °C. At 630 °C, the shift became 1°, and the diffraction line of $MgAl_2O_4$ appears. This shift indicates that LiF is strongly thermally expanded at the temperature of beginning of the formation of $MgAl_2O_4$.[2]

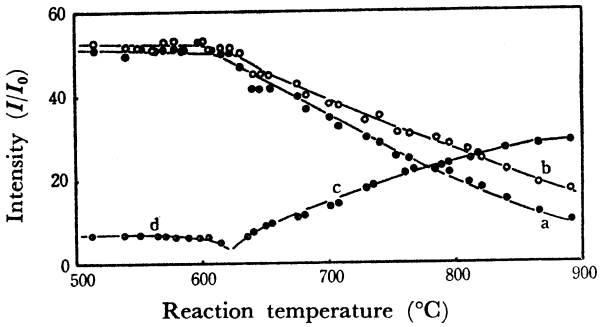

Fig. 1. High-temperature X-ray diffraction patterns of the reaction in MgO–Al_2O_3–LiF system. Molar mixing ratio: 1 : 1 : 0.2, Heating rate: 2—4 °C/min, in N_2 (300 mmHg).
a: α-Al_2O_3 (113), b: MgO (200), c: $MgAl_2O_4$ (400), d: LiF (200)

Figure 2 shows DTA curves (A: 1 : 1 : 0.2 mixture of MgO, Al_2O_3 and LiF in molar ratio) and X-ray diffraction patterns of the samples heated up to temperatures corresponding to points a and b on Curve A. The curve shows one endothermic peak 1 in the range 660—690 °C and one exothermic peak 2 in 690—750 °C. The cycles of heating and cooling of the sample for Curve A give endothermic and exothermic changes at 780—790 °C, respectively (Curve B). The samples containing LiF (0.5 molar ratio) showed DTA curves similar to Curves A and B. The DTA curves of MgO–LiF, Al_2O_3–LiF and MgO–Al_2O_3 systems, however, showed no thermal changes in the range 20—1000 °C except for the endothermic peak due to melting of LiF. It thus seems that only the ternary system of MgO,

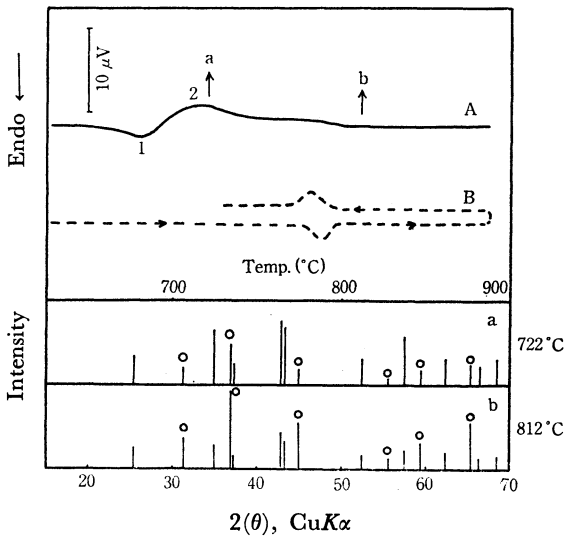

Fig. 2. DTA curve of the reaction in MgO–Al_2O_3–LiF system and X-ray diffraction patterns of the samples heated to a- and b-points. Heating rate: 10 °C/min, in N_2 (300 mmHg), sample weight: 300 mg.
A: 1 : 1 : 0.2 mixture of MgO, Al_2O_3 and LiF in molar ratio, B: heating and cooling cycle of sample for Curve A, ○: $MgAl_2O_4$

TABLE 1. THERMODYNAMIC DATA[a)]

$3LiF+2Al_2O_3=3LiAlO_2+AlF_3$	$\Delta H°=73$ kcal/mol
$3NaF+2Al_2O_3=3NaAlO_2+AlF_3$	$\Delta H°=76$ kcal/mol
$3MgF_2+4Al_2O_3=3MgAl_2O_4+2AlF_3$	$\Delta H°=111$ kcal/mol
$3CaF_2+4Al_2O_3=3CaAl_2O_4+2AlF_3$	$\Delta H°=210$ kcal/mol
$3BaF_2+4Al_2O_3=3BaAl_2O_4+2AlF_3$	$\Delta H°=$unknown
$MgO+2LiF=MgF_2+Li_2O$	$\Delta H°=30$ kcal/mol
$MgO+2NaF=MgF_2+Na_2O$	$\Delta H°=53$ kcal/mol
$MgO+CaF_2=MgF_2+CaO$	$\Delta H°=18$ kcal/mol
$MgO+BaF_2=MgF_2+BaO$	$\Delta H°=34$ kcal/mol
$3MgO+2AlF_3=3MgF_2+Al_2O_3$	$\Delta H°=-140$ kcal/mol
$MgO+2AlOF=MgF_2+Al_2O_3$	$\Delta H°=-243$ kcal/mol
$MgO+Al_2O_3=MgAl_2O_4$	$\Delta H°=-9.1$ kcal/mol

a) From Ref. 7.

Al_2O_3 and LiF shows peaks 1 and 2 (Curve A, Fig. 2). Peak 2 is probably related to the formation of $MgAl_2O_4$, since $MgAl_2O_4$ is formed at point a after peak 2 and $\Delta H°$ of this spinel formation is −9.1 kcal/mol (Table 1). At point b, a large amount of $MgAl_2O_4$ is also found to be formed. The reversible thermal changes of Curve B may be due to the formation of the liquid phase by the reaction in MgO–Al_2O_3–LiF system.

MgO–Al_2O_3–NaF System. Figure 3 shows the results of high-temperature X-ray analysis for the reaction of MgO–Al_2O_3–NaF system. The initiation of formation of $MgAl_2O_4$ is seen at 720 °C, a rapid increase in its amount with the rapid decrease in that of MgO and Al_2O_3 being observed. The temperature dependency leads to a large activation energy for the ΔH^* value formation of $MgAl_2O_4$. This is consistent with a ΔH^* value large (activation enthalpy).[1)] The thermal expansion of NaF is considered to be significant at 720 °C, since the large shift of diffraction line (200) to the

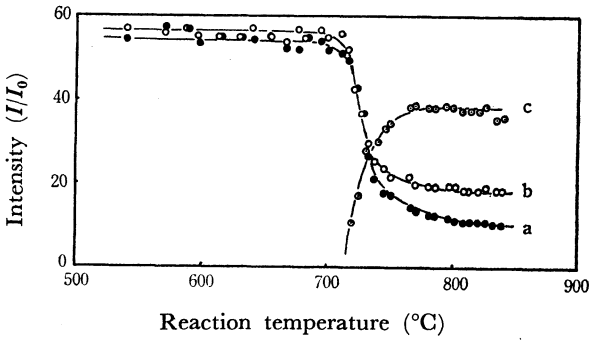

Fig. 3. High-temperature X-ray diffraction patterns of the reaction in MgO–Al_2O_3–NaF system. Molar mixing ratio: 1 : 1 : 0.2, Heating rate: 2—4 °C/min, in N_2 (300 mmHg).
a: α-Al_2O_3 (113), b: MgO (200), c: $MgAl_2O_4$ (400)

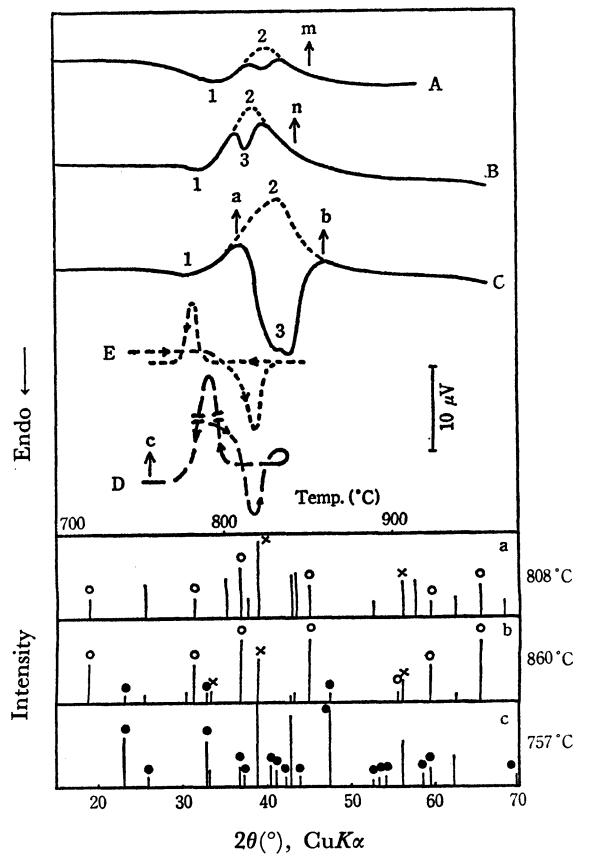

Fig. 4. DTA curves of the reaction in MgO–Al_2O_3–NaF system and X-ray diffraction patterns of the samples heated to a-, b- and c-points. Heating rate: 10 °C/min, in N_2 (300 mmHg), sample weight: 300 mg.
A: 1 : 1 : 0.1 mixture of MgO, Al_2O_3 and NaF in molar ratio, B: 1 : 1 : 0.2 mixture, C: 1 : 1 : 0.8 mixture, D: 1 : 1 mixture of MgF_2 and NaF in weight ratio, E: heating and cooling cycle of sample for Curve C
○: $MgAl_2O_4$, ×: NaF, ●: $NaMgF_3$
m: α=60%, n: α=55%

lower angle with temperature, similar to the case of LiF, was also observed for NaF.[3]

Figur 4 shows DTA curves and X-ray diffraction patterns of samples heated up to temperatures corresponding to points a, b and c on Curves C and D. The molar mixing ratios of MgO, Al_2O_3 and NaF for Curves A, B and C are: A, 1 : 1 : 0.1; B, 1 : 1 : 0.2; C, 1 : 1 : 0.8. Curve D was obtained from the 1 : 1 binary mixture (weight ratio) of MgF_2 and NaF, and Curve E from the sample used for Curve C after it had been heated up to 960 °C. Each curve of MgO–Al_2O_3–NaF systems shows an endothermic peak 1 in the range 760—795 °C and the overlap of an exothermic peak 2[4] with an endothermic peak 3. The DTA curves of binary systems such as MgO–NaF and Al_2O_3–NaF showed no thermal change except for the melting of NaF.

The fractional conversions of $MgAl_2O_4$ for the samples heated up to 852 °C (point m) on Curve A and up to 842 °C (point n) on Curve B were estimated to be α=60% and 55%, respectively. Comparable α values imply that the amount of $MgAl_2O_4$ produced does not necessarily depend on the amount of NaF added. The area of peak 2 seems to increase with the amount of NaF, suggesting peak 2 to contain another exothermic reaction in addition to $MgAl_2O_4$ formation. From X-ray diffraction patterns (Fig. 4), the presence of $NaMgF_3$, a complex compound formed from NaF and MgF_2,[5] is observed in addition to $MgAl_2O_4$ at point b on Curve C. Thus, it can be assumed that the exothermic peak 2 is due to the formation of $MgAl_2O_4$ and MgF_2. Peak 3 is considered to be due to the formation of liquid phase, since the cycles of heating and cooling of the sample for Curve C give endothermic and exothermic changes (Curve E). The two peak temperatures in Curve E are in agreement with those in Curve D obtained from MgF_2–NaF mixture, the temperatures being near the eutectic temperature of $NaMgF_3$ and NaF.[6] Thus, peak 3 might correspond to the melting of the mixture of $NaMgF_3$ and NaF. The results show that MgF_2 is formed in the MgO–Al_2O_3–NaF system, but not in the MgO–NaF system.

MgO–Al_2O_3–BaF_2 System. The results of high-temperature X-ray diffraction of this system are shown in Fig. 5. BaF_2 begins to decrease at *ca.* 680 °C (Curve d), and subsequently $MgAl_2O_4$ and $BaAl_2O_4$ begin to form near 700 °C (Curves c and e) with the simultaneous decrease of MgO and α–Al_2O_3 (Curves b and a). $BaAl_2O_4$ could be formed from the reaction of BaF_2 with α–Al_2O_3.

Figure 6 shows DTA curve (A: 1 : 1 : 0.5 mixture of MgO, Al_2O_3 and BaF_3 in molar ratio) and X-ray diffraction patterns of sample heated up to 870 °C (point a). Curve A shows similar thermal behaviors; a small endothermic peak 1, followed by an exothermic peak 2. DTA curves for the binary system of MgO–BaF_2 and Al_2O_3–BaF_2, however, showed no thermal change in the range 20—1100 °C. The cycles of heating and cooling of the sample for Curve A show no thermal change either. $MgAl_2O_4$ and $BaAl_2O_4$ were found to form at point a and the fractional conversion of $MgAl_2O_4$ was 63%. Thus peak 2 is related to the formation of $MgAl_2O_4$.

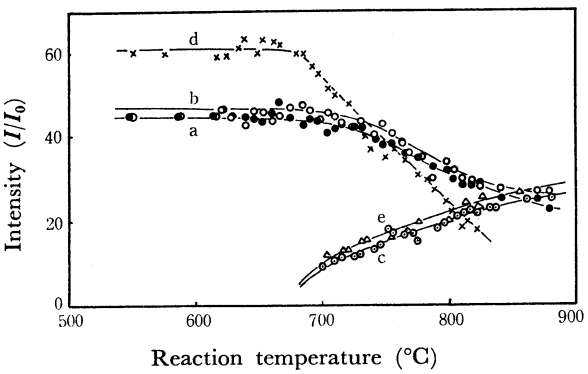

Fig. 5. High-temperature X-ray diffraction patterns of the reaction in MgO–Al_2O_3–BaF_2 system. Molar mixing ratio: 1 : 1 : 0.2, heating rate: 2—4 °C/min, in N_2 (300 mmHg).
a: α-Al_2O_3 (113), b: MgO (200), c: $MgAl_2O_4$ (400), d: BaF_2 (220), e: $BaAl_2O_4$ (112)

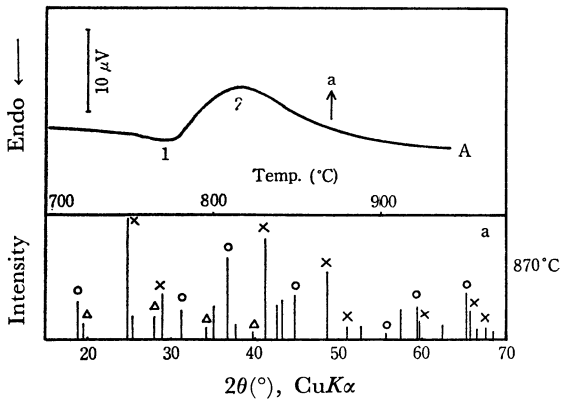

Fig. 6. DTA curve of reaction in MgO–Al_2O_3–BaF_2 system and X-ray diffraction patterns of the samples heated to a-point. Heating rate: 10 °C/min, in N_2 (300 mmHg), sample weight: 300 mg.
A: 1 : 1 : 0.5 mixture of MgO, Al_2O_3 and BaF_2 in molar ratio
△: $BaAl_2O_4$, ×: BaF_2, ○: $MgAl_2O_4$
a: α=63%

MgO–Al_2O_3–MgF_2 System. The high-temperature X-ray diffraction data are shown in Fig. 7. $MgAl_2O_4$ begins to form near 835 °C (Curve c) accompanied by the decrease of MgO, α-Al_2O_3 and MgF_2 (Curves b, a and d). The DTA curves in the MgO–Al_2O_3–MgF_2 and MgO–Al_2O_3–CaF_2 systems showed no thermal change in the range 20—1100 °C.

The Reaction of Fluorides with MgO and α-Al_2O_3. Peak 2 in Fig. 4 (MgO–Al_2O_3–NaF system) was found to correspond to the reaction, $MgO+Al_2O_3=MgAl_2O_4$ with $\Delta H°=-9.1$ kcal/mol, and to another extra exothermic reaction which seems to be MgF_2 formation from MgO and fluoride from the results of X-ray and DTA experiments. It was also found that the systems containing LiF (Fig. 2) and BaF_2 (Fig. 6) showed two peaks on the DTA curves similar to those of MgO–Al_2O_3–NaF system. Thus, peak 2 on the DTA curves of the systems containing LiF and BaF_2 is also assumed

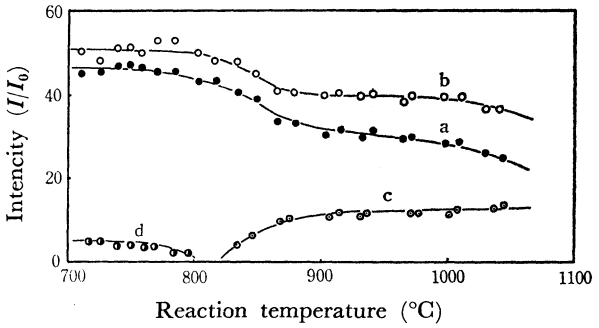

Fig. 7. High-temperature X-ray diffraction patterns of the reaction in $MgO-Al_2O_3-MgF_2$ system. Molar mixing ratio: 1 : 1 : 0.2, heating rate: 2—4 °C/min, in N_2 (300 mmHg).
a: α-Al_2O_3 (113), b: MgO (200), c: $MgAl_2O_4$ (400), d: MgF_2 (111)

to be due to the formation of MgF_2 and $MgAl_2O_4$, the latter being confirmed by X-ray analysis.

Three possible reactions, those of MgO with MF, AlOF or AlF_3, can be considered for MgF_2 formation (Table 1). However, the reactions of MgO with MF and AlOF can be excluded, since $\Delta H°$, the heat of the reaction of MgO with MF is positive, *viz.*, endothermic and experimental evidence for AlOF formation at temperatures below 1700 °C has not been reported.[8] Thus, it is reasonable to assume that MgF_2 is formed by the reaction

$$3MgO + 2AlF_3 = 3MgF_2 + Al_2O_3 \quad (1)$$

where AlF_3 is endothermally formed from Al_2O_3 and fluoride (Table 1). Thus the endothermic peak 1, which precedes peak 2, would be due to the reaction of α-Al_2O_3 with fluoride. On the other hand, the binary systems, Al_2O_3–fluoride, showed neither thermal changes in DTA curves nor X-ray diffraction lines of AlF_3. The results lead to an assumption that AlF_3 is formed from Al_2O_3 and fluoride in the presence of MgO in the temperature range 20—1000 °C. The reactions considered possible for peak 1 are as follows.

$$2Al_2O_3 + 3M^{I}F \xrightarrow{MgO} 3M^{I}AlO_2 + AlF_3 \quad (2)$$

$$4Al_2O_3 + 6M^{I}F \xrightarrow{MgO} 3M_2^{I}Al_2O_4 + 2AlF_3 \quad (2')$$

$$4Al_2O_3 + 3M^{II}F_2 \xrightarrow{MgO} 3M^{II}Al_2O_4 + 2AlF_3 \quad (3)$$

Formation of $M^{II}Al_2O_4$ was observed in the BaF_2–Al_2O_3–MgO system ($BaAl_2O_4$), and $NaAl_{11}O_{17}$, assumed to result from $M_2^{I}Al_2O_4$ ($Na_2Al_2O_4$) and Al_2O_3, was found in NaF–Al_2O_3–MgO system when NaF was sandwiched between MgO was Al_2O_3 pellets.[1]

AlF_3 was not found in any system examined directly by X-ray. This might be due to the small amount of fluoride additives and the easily occurring sublimation of AlF_3.[9] In order to examine the effects of AlF_3 resulting from Reaction (2)—(3), experiments were carried out for $MgO-Al_2O_3-AlF_3$ and $MgO-AlF_3$ system. Figure 8 shows DTA curves (A: $MgO-Al_2O_3-AlF_3$ system; B: $MgO-AlF_3$ system) and X-ray diffraction patterns. $AlF_3 \cdot H_2O$ used as starting material was subjected to dehydration in order to obtain anhydride AlF_3

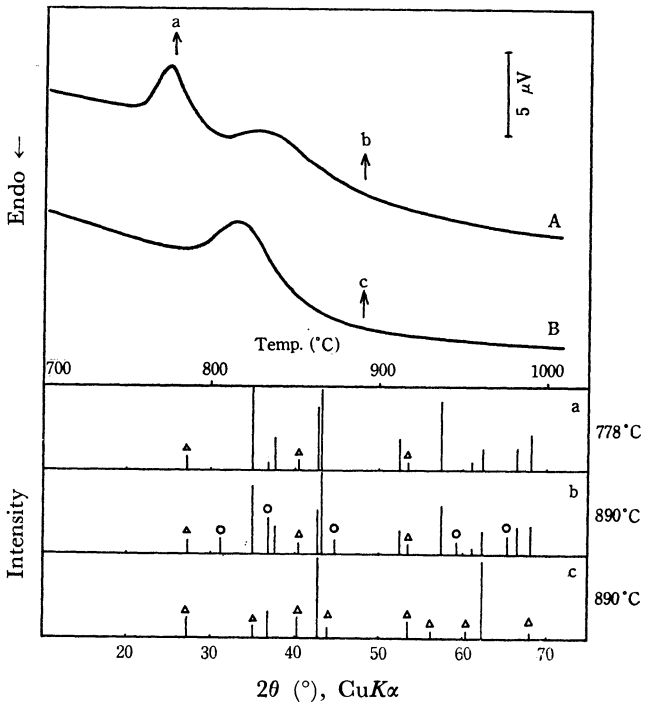

Fig. 8. DTA curves of the reaction in $MgO-Al_2O_3-AlF_3$ and $MgO-AlF_3$ systems, and X-ray diffraction patterns of the samples heated to a-, b- and c-points. Heating rate: 10°C/min, in N_2 (300 mmHg), sample weight: 300 mg.
○: $MgAl_2O_4$, △: MgF_2
a: α=0, b: α=32%

at 200—300 °C. $MgO-AlF_3$ system (Curve B) shows an exothermic peak due to Reaction (1) at 790—850 °C, since X-ray analysis indicated the formation of MgF_2 after this peak (point c). Curve A shows two exothermic peaks in the ranges 750—800 °C and 800—870 °C; the first corresponds to the exothermic peak on Curve B since only MgF_2 is formed at point a on Curve A; the second peak might be due to the formation of $MgAl_2O_4$, since $MgAl_2O_4$ was found to form at point b. It is thought that two exothermic peaks on Curve A can be associated with reaction of the exothermic peak 2 (Figs. 2, 4 and 6). The conversion of $MgAl_2O_4$ at point b (890 °C) was estimated to be α=32%. This

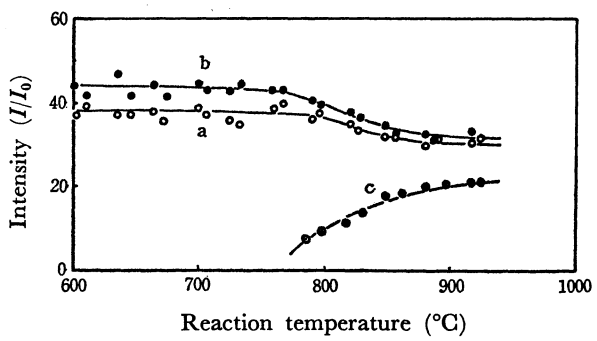

Fig. 9. High-temperature X-ray diffraction patterns of the reaction in $MgO-Al_2O_3-AlF_3$ system. Molar mixing ratio: 1 : 1 : 0.2, heating rate: 2—4 °C/min, in N_2 (300 mmHg).
a: α-Al_2O_3 (113), b: MgO (200), c: $MgAl_2O_4$ (400)

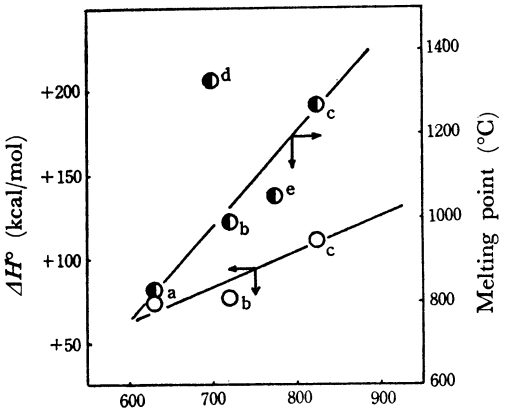

Fig. 10. Plots of $\Delta H°$ for the reactions in Table 1 and the melting points of fluorides *vs.* the initiation temperature of $MgAl_2O_4$ formation.
a: LiF, b: NaF, c: MgF_2, d: BaF_2, e: AlF_3

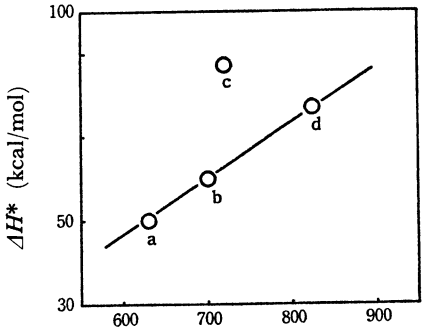

Fig. 11. Plots of activation enthalpy ΔH^* *vs.* the initiation temperatures of $MgAl_2O_4$ formation.
a: LiF, b: BaF_2, c: NaF, d: MgF_2

is comparable with $\alpha=20$—30%, the values corresponding to the rapid $MgAl_2O_4$ formation observed in the initial stage of isothermal experiments.[1] It seems from the data of MgO–Al_2O_3–AlF_3 (Fig. 9) that the presence of AlF_3 promotes the formation of $MgAl_2O_4$ as much as alkali and alkaline earth fluorides.

The formation of $MgAl_2O_4$ might be initiated by the presence of fluorides which form AlF_3 (Eqs. (2) and (3)), although each fluoride gives different initiation temperatures (Fig. 10). We see that the lower the value of $\Delta H°$ for Eqs. (2) and (3), the lower the initiation temperature of $MgAl_2O_4$ formation which can be determined by the high-temperature X-ray diffraction. We also see that the lower the melting point of the fluoride[10] except for point d (BaF_2), the lower the initiation temperature. This seems to be correlated to the strong thermal expansion of the crystalline lattices of LiF and NaF: the thermal vibration of these fluorides lattices is enhanced by the rise in temperature, and the exchange reaction between F^- and O^{-2} on the surface of α-Al_2O_3 and/or MgO particles occurs to form AlF_3. This might influence the surface of α-Al_2O_3 and MgO particles and causes the reaction between MgO and α-Al_2O_3 leading to the formation of $MgAl_2O_4$. The deviation of point d from the straight line (Fig. 10) cannot be explained at present.

The cations of fluoride play an important role in the enhancement of diffusion rate.[1] If the activation enthalpy (Table 2, Ref. 1) can be taken as a relative measure of the ease of the occurrence of reaction, it is expected that the smaller the activation enthalpy, the lower the initiation temperature of the formation of $MgAl_2O_4$. This is satisfied in Fig. 11 except for point c. Accordingly, it can be assumed that the initiation temperature of $MgAl_2O_4$ formation is lowered by the incorporation of Reactions (1), (2) and (3) with the reaction between MgO and α-Al_2O_3.

References

1) S. Shimada, R. Furuichi, and T. Ishii, This Bulletin, **47**, 2026 (1974).
2) The shift at 630 °C calculated by using the coefficient of expansion of LiF, $\alpha=3.4\times10^{-5}/K$[11] turned out to be 0.9°, which is comparable with the observed value.
3) The shift at 650 °C calculated by using $\alpha=3.6\times10^{-5}/K$[11], 1.0 was comparable with the observed value 0.7.
4) Peak 2 (dotted line) was drawn by assuming that it resulted from the reaction of $2AlF_3+3MgO=3MgF_2+Al_2O_3$ (Table 1).
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