Effects of Additives on Solid State Reaction. III. Effects of Halide Additives on the Formation of $MgFe_2O_4$

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The promoting effects of halide additives on the formation of $MgFe_2O_4$ have been studied on the basis of both kinetic and thermoanalytical data. A mixture of MgO and α-Fe_2O_3 powder containing 10 mol % additive (LiF, NaF, MgF_2, BaF_2, NaCl, or KCl) and that without additive were isothermally heated in a vacuum ($P_{O_2}=10^0$—10^1 mmHg) in the temperature range 666—1018 °C. High temperature X-ray analysis on MgO–Fe_2O_3 and MgO–Fe_2O_3–additive systems was carried out at a heating rate of 3 °C/min *in vacuo*, ($P_{O_2}=10^{-1}$ mmHg). In the case of fluoride, it seems that the reactions between the fluoride and the reactants, α-Fe_2O_3 or MgO, promote $MgFe_2O_4$ formation in the initial stage and that compounds produced by the initial reaction accelerate diffusion in the later stage. The same promoting mechanism seems to be applicable to the case of chloride additives. The interaction between solids of NaCl and α-Fe_2O_3 occurring just before the melting of NaCl seems to initiate $MgFe_2O_4$ formation.

Solid state reactions are affected by various factors such as impurity or additive,[1,2] preparation history of the reacting material[3] and atmosphere.[4-6] The mechanism for the promoting effects of fluoride and chloride additives on $MgAl_2O_4$ formation has been systematically discussed from kinetic and thermoanalytical viewpoints.[7-9] In the case of fluoride additives,[8,9] the formation of $MgAl_2O_4$ was initiated by the reaction between fluoride and reactants of α-Al_2O_3 and MgO, the cations of fluoride playing an important role in accelerating the reaction in the later stage. In the case of chloride,[7,8] the $MgAl_2O_4$ formation was accelerated *via* the dissolution process of MgO particle in molten chloride.

We have investigated the promoting effects of the halides of alkali and alkaline earth on $MgFe_2O_4$ formation on the basis of both kinetic and thermoanalytical results.

Experimental

Sample. α-Fe_2O_3 samples were prepared by calcining commercial ferric oxide (Kanto Chemical Co., 99% pure) at 1100 °C in the air. The particle size of α-Fe_2O_3 was microscopically determined to be in the range 0.5—2 μ with an average size of 1 μ. MgO particles (av. 0.1 μ) were prepared by a similar way to that described in the previous paper.[8] Powders of MgO, α-Fe_2O_3 and additive were thoroughly mixed in the molar ratio 1 : 1 : 0.1. The additives used were LiF, NaF, MgF_2, BaF_2, NaCl, or KCl (Kanto, Wako or Morita Companies), which were stored in a desiccator with silica gel before experiments. The mixtures were pressed into pellets at 150 kg/cm^2.

DTA and High Temperature X-Ray Diffraction Experiments. DTA experiments on MgO–Fe_2O_3 and MgO–Fe_2O_3–additive systems were carried out in a vacuum ($P_{O_2}=10^{-1}$ mmHg) at a heating rate of 10 °C/min. The temperature was measured with a Pt–Pt13Rh thermocouple. α-Al_2O_3 was used as a standard material. The high temperature X-ray diffraction experiments were carried out *in vacuo* ($P_{O_2}=10^{-1}$ mmHg) at a heating rate of 3 °C/min.

Isothermal Kinetic Experiments. The pellet was kept on a Pt boat placed in a fused-silica tube connected to a vacuum system ($P_{O_2}=10^0$—10^1 mmHg) and then heated isothermally in the Pt-furnace at 666—1018 °C. The temperature was measured with a Pt–Pt13Rh thermocouple. After heating, the pellet was quenched at room temperature by withdrawal of the tube from the hot zone of the furnace. Fractional conversion of $MgFe_2O_4$ was determined by measuring the amount of MgO or α-Fe_2O_3 remaining after the reaction. The MgO unreacted was extracted by dissolving the pellet in 10% NH_4Cl solution. The Mg^{2+} ion concentration of the solution was then determined by titration with a standard solution of EDTA. This procedure was applied to the products obtained in the experiments of both MgO–Fe_2O_3 and MgO–Fe_2O_3–additive (LiF or NaF) systems. The amount of α-Fe_2O_3 unreacted was determined by quantitative X-ray analysis by use of NaCl as an external standard. The method was applied to the products in MgO–Fe_2O_3–additive (MgF_2 or BaF_2) system.

Analyis of Fe^{2+}. The amount of Fe^{2+} ion in the samples, obtained after isothermal experiments or the high temperature X-ray diffraction experiments, was colorimetrically determined.[10] The solution for colorimetry was prepared by dissolving the sample in concd H_2SO_4. 2M NH_4F and 1% *o*-phenanthroline were used as masking agent for Fe^{3+} and color-producing agent for Fe^{2+}.

Results

Figures 1 and 2 show the rates of $MgFe_2O_4$ formation in MgO–Fe_2O_3 and MgO–Fe_2O_3–alkali fluoride systems, and MgO–Fe_2O_3–alkaline earth fluoride system, respectively. The rate of reaction between solid reactant particles is generally governed by either chemical reaction at phase-boundary or diffusion process.[11] The rate equations for the diffusion-controlled reaction have been given by Jander,[12] Serin-Ellickson,[13] Ginstling-Brounshtein,[14] and Carter.[15] It was found that the reaction rate of MgO–Fe_2O_3 system is best represented by Jander's equation:

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

where α=fractional conversion, k=rate constant, t=reaction time. A part of the data plotted according to Eq. (1) is shown in Fig. 3. We see that the data of all systems fit Jander's equation up to about $\alpha=70\%$. The straight lines obtained for NaF, MgF_2 and BaF_2 additives intersect at $t=0$ the ordinate with values corresponding to $\alpha=20$—30%. On the other hand, the lines for non-additive and LiF additive fall on the origin. The activation energies are given in Table 1,

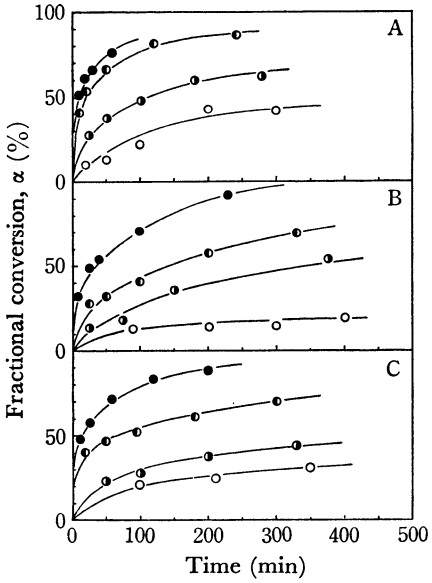

Fig. 1. Formation rate of $MgFe_2O_4$ for MgO–Fe_2O_3 and MgO–Fe_2O_3–alkali fluoride systems.
A: MgO–Fe_2O_3 system
○: 853 °C, ◑: 915 °C, ◐: 972 °C, ●: 1018 °C
B: MgO–Fe_2O_3–LiF system
○: 666 °C, ◑: 715 °C, ◐: 760 °C, ●: 814 °C
C: MgO–Fe_2O_3–NaF system
○: 754 °C, ◑: 798 °C, ◐: 850 °C, ●: 901 °C

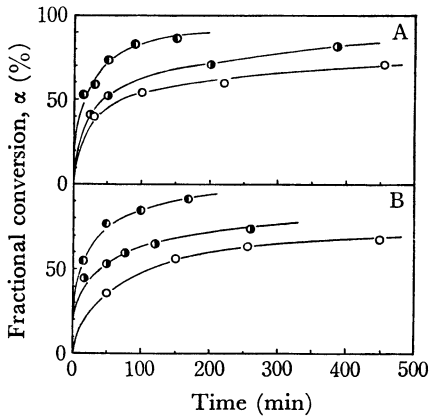

Fig. 2. Formation rate of $MgFe_2O_4$ for MgO–Fe_2O_3–alkaline earth fluoride system.
A: MgO–Fe_2O_3–MgF_2 system
○: 847 °C, ◑: 895 °C, ◐: 940 °C
B: MgO–Fe_2O_3–BaF_2 system
○: 847 °C, ◑: 895 °C, ◐: 940 °C

for which the rate constants k were calculated from the results shown in Figs. 1 and 2 by means of Eq. (1). The samples obtained by the isothermal experiments of all systems showed no trace of Fe^{2+}.

Figure 4 shows DTA curves of MgO–Fe_2O_3–LiF (curve A) and MgO–Fe_2O_3–NaF (curve B) systems. Curve A has two endothermic peaks at 670 °C and 730 °C. The peak at 730 °C is considered to be due to the formation of the liquid phase, since an exothermic peak was obtained at *ca.* 730 °C by cooling the sample (curve A) from 930 °C as indicated by arrows. The liquid phase seems to result from melting of LiF.

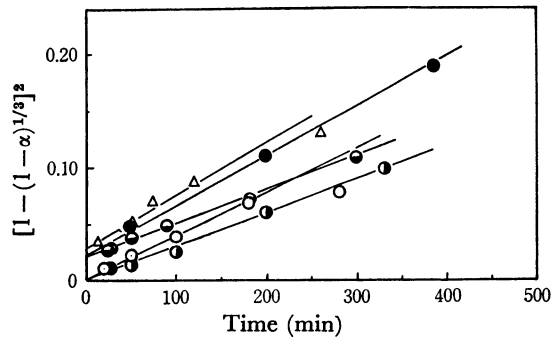

Fig. 3. Plots of $[1-(1-\alpha)^{1/3}]^2$ *vs.* t according to the Jander's equation.
○: non-additive (915 °C), ◑: LiF (760 °C), ◒: NaF (850 °C) ●: MgF_2 (895 °C), △: BaF_2 (895 °C)

Table 1. Values of activation energy

Additive	E^* (kcal/mol)
Non-additive	70± 4
LiF	57± 4
NaF	59± 4
MgF_2	65±10
BaF_2	60± 5

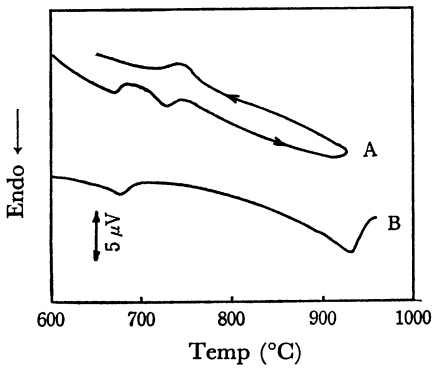

Fig. 4. DTA curves of reaction in MgO–Fe_2O_3–LiF (curve A) and MgO–Fe_2O_3–NaF (curve B) systems. Heating rate: 10 °C/min, sample weight: 400 mg, 1:1:0.1 mixture of MgO, Fe_2O_3, and LiF or NaF in molar ratio.

Similarly, curve B has two endothermic peaks at 670 °C and 930 °C. The peak at 930 °C probably corresponds to melting of NaF. DTA curves of the systems with non-additive, MgF_2 and BaF_2 additives showed no thermal change in the range 20—1000 °C except for the endothermic peak near 670 °C, which showed a reversible one. This peak corresponds to the Curie point of α-Fe_2O_3.[16,17]

Figures 5A-D and 6A-D show the results of high temperature X-ray diffraction analysis for the systems MgO–Fe_2O_3, MgO–Fe_2O_3–NaCl, MgO–Fe_2O_3–KCl, Fe_2O_3–NaCl, MgO–Fe_2O_3–LiF, MgO–Fe_2O_3–NaF, MgO–Fe_2O_3–MgF_2, and MgO–Fe_2O_3–BaF_2. We see that the amounts of α-Fe_2O_3 and MgO decrease at *ca.* 700 °C and then $MgFe_2O_4$ begins to appear at 820 °C (Fig. 5-A). Addition of NaCl (Fig. 5-B) lowers the initiation temperature of $MgFe_2O_4$ formation by more than 60 °C, as compared with that of the MgO–Fe_2O_3 system. This initiation temperature, 760 °C, is lower

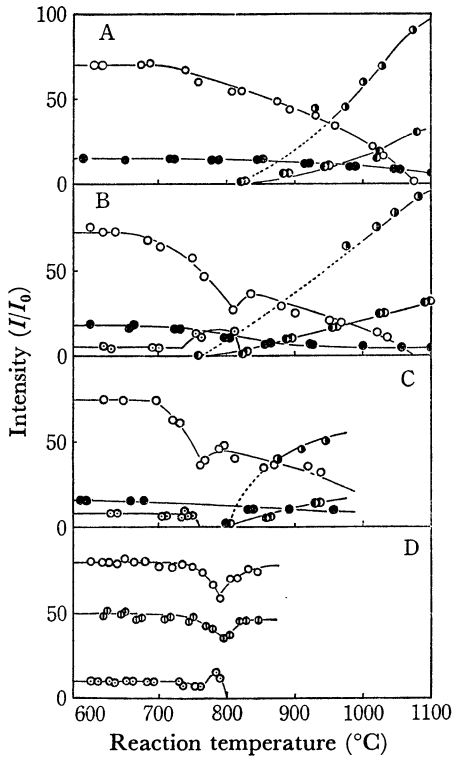

Fig. 5. High temperature X-ray diffraction patterns of the reaction in the systems for MgO–Fe_2O_3 (A), MgO–Fe_2O_3–NaCl (B), MgO–Fe_2O_3–KCl (C), and Fe_2O_3–NaCl (D).
Molar mixing ratio: 1: 1: 0.1 in MgO: Fe_2O_3: chloride and 1: 0.2 in Fe_2O_3: NaCl, heating rate: 3 °C/min.
○: α-Fe_2O_3 (104), ●: MgO (200), ◑ and ◐: Mg-Fe_2O_4 (311) and (200), respectively, B-⊙: NaCl (200), C-⊙: KCl (200), D-ⓘ, -○ and -⊙: α-Fe_2O_3 (104), α-Fe_2O_3 (110) and NaCl (200), respectively.

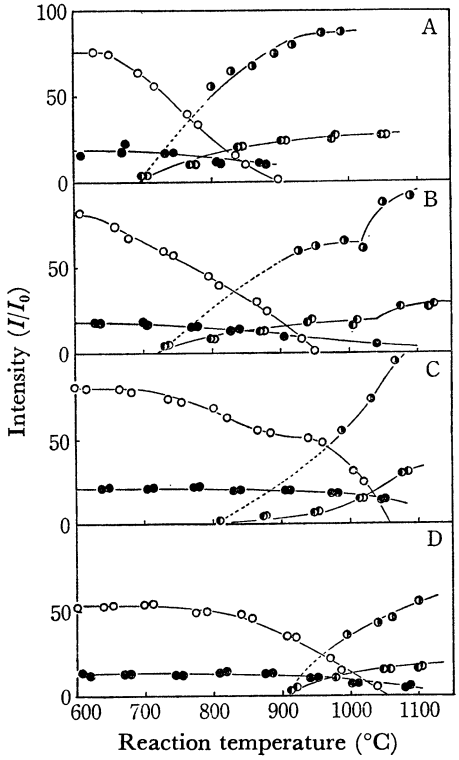

Fig. 6. High temperature X-ray diffraction patterns of the reaction in systems for MgO–Fe_2O_3–LiF (A), MgO–Fe_2O_3–NaF (B), MgO–Fe_2O_3–MgF_2 (C) and MgO–Fe_2O_3–BaF_2 (D).
Molar mixing ratio: 1: 1: 0.1, heating rate: 3 °C/min
○: α-Fe_2O_3 (104), ●: MgO (200), ◑ and ◐: Mg-Fe_2O_4 (311) and (200), respectively

than the melting point of NaCl (mp 808 °C). In the case of KCl (Fig. 5-C), $MgFe_2O_4$ begins to form at *ca.* 800 °C after melting of KCl (mp 776 °C). The discontinuous changes in the X-ray intensities of α-Fe_2O_3 and NaCl for MgO–Fe_2O_3–NaCl system (Fig. 5-B), and of α-Fe_2O_3 for MgO–Fe_2O_3–KCl system (Fig. 5-C) are observed just before the melting of chloride additives. Such phenomena are also observed in the binary system of NaCl–Fe_2O_3 (Fig. 5-D). Addition of LiF (Fig. 6-A) lowers the initiation temperature of $MgFe_2O_4$ formation to 700 °C. This temperature is close to that of the liquid phase formation (730 °C) in MgO–Fe_2O_3–LiF system (Fig. 4). In the case of NaF (Fig. 6-B), the initiation temperature is also lowered, the intensity of $MgFe_2O_4$ increasing abruptly at 1020 °C.

Table 2. The initiation temperature of $MgFe_2O_4$ formation

Additive	Init. temp (°C)
Non-additive	820
LiF	700
NaF	725
MgF_2	800
BaF_2	900
NaCl	760
KCl	800

In the case of MgF_2 (Fig. 6-C), $MgFe_2O_4$ begins to form at 800 °C. On the other hand, the initiation temperature of the system with BaF_2 (Fig. 6-D) is somewhat higher in comparison with that of other systems. The initiation temperatures of the $MgFe_2O_4$ formation in all the systems are summarized in Table 2. It is seen that α-Fe_2O_3 in MgO–Fe_2O_3 system disappears at temperatures higher than 1075 °C, but MgO still exists at these temperatures (Fig. 5-A). Similar phenomena are also observed at 1075 °C, 950 °C, 1060 °C, or 1050 °C in MgO–Fe_2O_3–NaCl, –NaF, –MgF_2, or –BaF_2, respectively. The samples obtained after the high temperature X-ray diffraction experiments (Figs. 5-A, -B and 6-A, -B, -C, -D) showed traces of Fe^{2+}.

Discussion

It was found[9] that the lower the melting point of the fluoride additives, the lower the initial temperature of $MgAl_2O_4$ formation, and that AlF_3 formed by the reaction between fluorides and α-Al_2O_3 initiates the formation of $MgAl_2O_4$. For the MgO–Fe_2O_3–fluoride systems, a linear correlation of the melting point of the fluoride with the initiation temperature of $MgFe_2O_4$ formation (Table 1) was also observed (Fig. 7). Deviation of the point for BaF_2 from a straight line may be due to the poor crystallinity of $MgFe_2O_4$ formed, since although the initial temperature of $MgFe_2O_4$ formation is at *ca.* 900 °C (Fig. 6-D), the fractional conversion

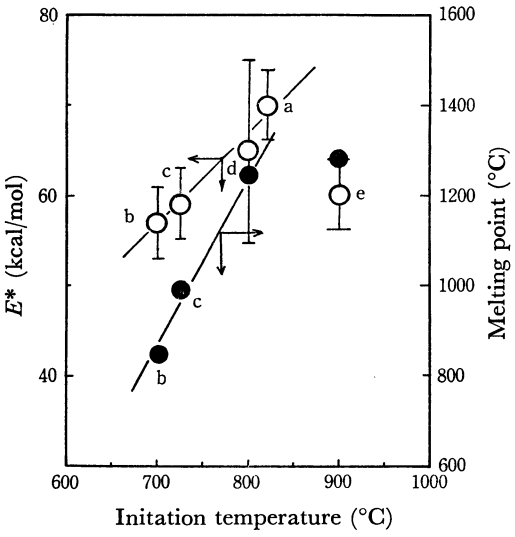

Fig. 7. Plots of the melting points of halide and the E^* values *vs.* the initiation temperature of $MgFe_2O_4$ formation.
a: non-additive, b: LiF, c: NaF, d: MgF_2, e: BaF_2

determined from the amount of unreacted α-Fe_2O_3 after the isothermal experiments goes up to $\alpha=36\%$ at 847 °C for 50 min in MgO–Fe_2O_3–BaF_2 system. The correlation in Fig. 7 suggests that the fluoride of lower melting point easily reacts with reactants α-Fe_2O_3 or MgO and that the reaction promotes the $MgFe_2O_4$ formation in the initial stage, as described for MgO–Al_2O_3–fluoride system. The reaction of fluoride with reactants may result in the formation of compounds such as magnesium or iron fluoride. The formation of such compounds results in the lowering of the melting point of LiF (mp 845 °C) or NaF (mp 992 °C) by more than 100 °C or 60 °C, respectively (Fig. 4). On the other hand, the melting point of the binary systems such as MgO–LiF or –NaF and Fe_2O_3–LiF or –NaF nearly agreed with that of pure LiF or NaF. However, X-ray analysis for the products obtained in the DTA experiments did not indicate the formation of compounds such as magnesium or iron fluoride, or Li–, Na–, or Ba–ferrite. This might be due to too small amounts of the compounds for detection by X-ray analysis.

Reijnen[18] studied the solid state reaction in the MgO–Fe_2O_3 system, and proposed two possible mechanisms of counter diffusion of cations for the formation of $MgFe_2O_4$ at a given oxygen pressure and temperature, *i.e.* Mg^{2+} and Fe^{3+}, or Mg^{2+} and Fe^{3+} or Fe^{2+} diffuse through the spinel layer. The Fe^{2+} diffusion is accompanied by the diffusion of one cation vacancy and by the transport of oxygen in the gas phase. Carter[19] assumed the mechanism of the counter diffusion of Mg^{2+} and Fe^{3+}. Lindner[20,21] reported that the activation energy for the self-diffusion of Mg^{2+} in MgO single crystal is 79 kcal/mol and that of Fe^{3+} in $ZnFe_2O_4$ polycrystal is 82 kcal/mol. These can be regarded as values for the volume or grain boundary diffusion. It was found from the results given in Fig. 3 and Table 1 that the formation rate of $MgFe_2O_4$ in MgO–Fe_2O_3 system is controlled by the diffusion with the activation energy of 70 ± 4 kcal/mol, which is comparable to the above values. Since no Fe^{2+} was found in the samples obtained by the isothermal experiments, it seems that $MgFe_2O_4$ formation in MgO–Fe_2O_3 system proceeds by the counter diffusion of Mg^{2+} and Fe^{3+} and that the volume or grain-boundary diffusion is operative in the formation of $MgFe_2O_4$. The presence of fluorides lowers the value of the activation energy E^* by 5—13 kcal/mol (Table 1), which might indicate that the fluorides accelerate the diffusion along grain boundary or within bulk. There is a possibility that the dissolution or incorporation of compounds formed by the reaction of fluoride with α-Fe_2O_3 into the $MgFe_2O_4$ layer facilitates the diffusion of Mg^{2+} or Fe^{3+}. It can be considered in the case of LiF or NaF additive that the liquid phase formation at *ca.* 700 °C or 800 °C accelerates further diffusion by acting as a vehicle of transporting MgO or α-Fe_2O_3. It is observed that the lower the E^* value, the lower the initiation temperature of $MgFe_2O_4$ formation (Fig. 7).

The accelerating mechanism of $MgFe_2O_4$ formation by the presence of chloride was explained as follows: MgO particles dissolve in molten chloride to spread uniformly over the outer surface of α-Al_2O_3 particles and then MgO particles transport into the inner part of α-Al_2O_3 particles consisting of crystallites. In the MgO–Fe_2O_3–NaCl system, discontinuous changes in X-ray diffraction intensities of α-Fe_2O_3 and NaCl were observed before melting of NaCl, the initial for mation of $MgFe_2O_4$ beginning simultaneously (Fig. 5-B). The discontinuous changes of X-ray intensities seem responsible for the initial formation of $MgFe_2O_4$, although no explanation can be given at present. In the case of KCl, $MgFe_2O_4$ was formed after melting of KCl, although a discontinuous change of α-Fe_2O_3 intensity was also observed (Fig. 5-C). There may be a difference in the action of solids NaCl and KCl on the $MgFe_2O_4$ formation. It is considered that after chloride melts, the formation of $MgFe_2O_4$ is promoted by the dissolution process of MgO particles in molten chloride.

It was found in the high temperature X-ray experiments that α-Fe_2O_3 disappears at temperatures where MgO still exists (Figs. 5 and 6) and that a trace of Fe^{2+} is present in the samples after the experiments. This suggests that a part of Fe^{3+} is reduced at high temperatures to ferrous ions by the dissolution of α-Pe_2O_3 in $MgFe_2O_4$ phase at relatively high vacuum ($Po_2=10^{-1}$ mmHg) in comparison with that in the isothermal experiments ($Po_2=10^0$—10^1 mmHg), and that the $MgFe_2O_4$ formation proceeds by the counter diffusion mechanism of Mg^{2+} and Fe^{3+} accompanied by partial participation of Fe^{2+} in the diffusion, as proposed by Reijnen.[18]

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