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Influence of fluorine ion on the spinel synthesis

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The beneficial influence of mineralizers on the development of solid-state processes has been recognized for a long time [1]. However, the mechanisms of this influence are more or less unknown. The results obtained during the investigation of $MgAl_2O_4$ synthesis showed that in the presence of small amounts of AlF_3 and CaF_2, the rate of spinel formation in the $MgO–Al_2O_3$ system was substantially increased. In this paper the mechanism of AlF_3 and CaF_2 influence on the spinel synthesis is described.

The starting materials for $MgAl_2O_4$ synthesis were Al_2O_3 and $MgCO_3$. The properties of the powders are given in Table I. The corresponding mixtures of Al_2O_3 and $MgCO_3$ with and without mineralizer, were pressed under 78.5 MPa and thereafter, heated in the temperature range 1100 to 1400° C. The reaction degree after the heating of the samples was determined using X-ray analysis, by comparing the diffraction line intensities of spinel in the samples, with the intensity of diffraction lines of fully reacted spinel.

With the pure mixture Al_2O_3 and MgO (molar ratio 1:1) 67% of spinel phase was formed at 1400° C, after 4 h of isothermal heating. By adding 0.75% and 1.75% of AlF_3 to the same starting mixture, the amount of formed spinel was considerably higher, as compared to the mixture of Al_2O_3 and MgO without mineralizer. The obtained results are shown in Table II. The influence of different concentrations of AlF_3 on the $MgAl_2O_4$ formation is even better illustrated by the data in Fig. 1. These results were obtained by heating at 1000° C.

After heating green pellets of pure Al_2O_3–MgO mixture at 1100° C for 2 h in loose CaF_2 and loose AlF_3 powders, it was found that with samples packed in CaF_2 loose powder, 68% spinel was formed. On the other hand, with samples heated in AlF_3 loose powder the amount of spinel phase was approximately 0 wt %.

Simultaneously, the investigation of the influence of AlF_3 on $\gamma \rightarrow \alpha$ transition in Al_2O_3 was followed. DTA results are shown in Fig. 2. It is obvious that in the presence of AlF_3 the temperature of $\gamma \rightarrow \alpha$ transition can be lowered by 140° C. The DTA curves were obtained under identical experimental conditions (heating rate $10° \min^{-1}$, sensitivity $10 \mu V$).

The analysis of the obtained results on the influence of investigated mineralizers either on

TABLE I Characteristics of the powders used for $MgAl_2O_4$ synthesis

Property	Al_2O_3	$MgCO_3$
Chemical composition (wt %)		
Al_2O_3	99.42	0.01
SiO_2	0.08–0.12	0.46
Fe_2O_3	0.05–0.06	0.17
CaO	–	0.64
MgO	–	47.75
Specific surface area ($m^2 g^{-1}$)	1.57	–
Loss on ignition up to 1000° C (wt %)	–	52.25

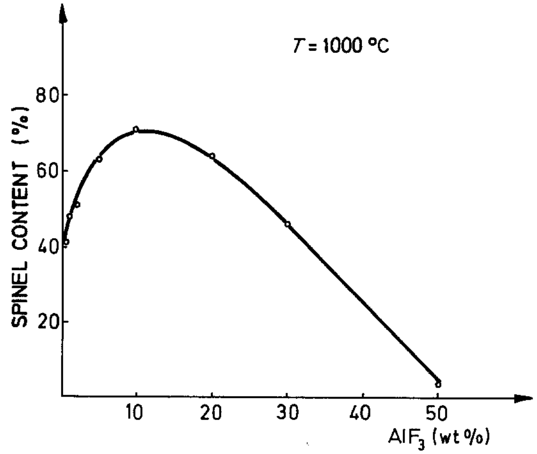

Figure 1 The amount of spinel as a function of AlF_3 concentration in the Al_2O_3–MgO mixture at 1000° C.

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TABLE II The amount of $MgAl_2O_4$ in the presence of AlF_3 (wt%)

AlF_3 (wt%)	1100° C		1200° C		1300° C		1400° C	
	2 h	4 h	2 h	4 h	2 h	4 h	2 h	4 h
0.75	85	86	93	–	94	–	95	–
1.75	89	97	94	–	95	–	96	–

spinel synthesis or on $\gamma \rightarrow \alpha$ transition in Al_2O_3 point to the conclusion that the fluorine ion must exhibit a substantial effect on the rate of the mentioned solid-state processes.

At the same time, the results indicated that the fluorine ion affected the process of spinel synthesis through Al_2O_3 component. To prove this assumption the synthesis was followed in different systems containing Al_2O_3 as a reactant. The results we obtained are given in Table III. It is obvious (Table III) that besides with MgO, the reactions of Al_2O_3 with Y_2O_3, Dy_2O_3 and SiO_2 are enhanced in the presence of AlF_3 as well.

On the basis of the ionic radii values (F^- –0.136 nm, O^{2-} –0.176 nm) it is concluded that F^- can be incorporated in the anion sublattice. Bearing in mind the mechanism of $MgAl_2O_4$ formation [2], the fluorine ion can make the movement of cations through the Al_2O_3 and $MgAl_2O_4$ lattice easier. This is the consequence of the increased concentration of cation vacancies within both Al_2O_3 and $MgAl_2O_4$.

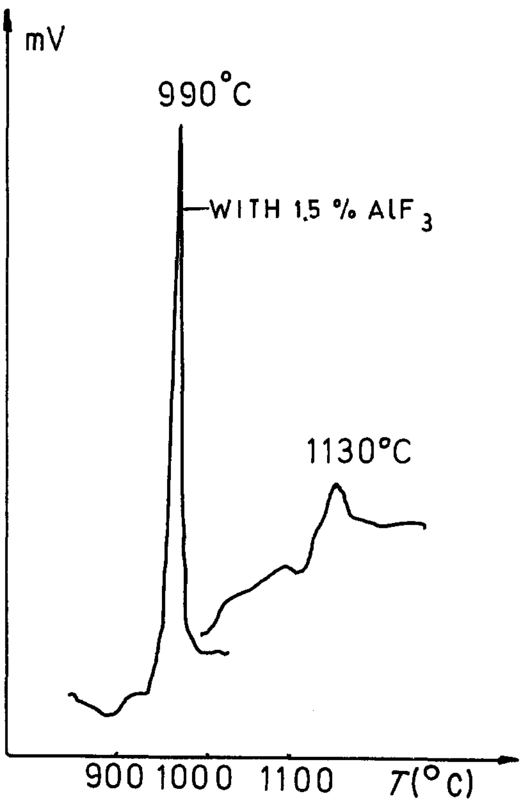

Figure 2 DTA curves showing $\gamma \rightarrow \alpha$ transition in Al_2O_3 with and without mineralizers.

The thermogravimetry curve for pure AlF_3 (Fig. 3) already shows a weight loss at 700° C that can be ascribed to F^- ion release. The process of AlF_3 decomposition takes place very rapidly in the temperature range 1100 to 1200° C (Fig. 3). In this temperature range, having in mind data in Table II, the enhanced dissolution of F^- ion in Al_2O_3 and $MgAl_2O_4$ lattices can be expected, too. X-ray analysis of AlF_3 heated up to 1200° C showed the presence of Al_2O_3 besides the lines of AlF_3 of very small intensity. TG analysis of CaF_2 showed that the overall weight loss during heating up to 1200° C, was only 2.57 wt %.

F^- ion incorporated in the lattice instead of O^{2-} ion, creates cation vacancies in the bulk. As a consequence, the cation diffusion through both Al_2O_3 and spinel lattices will be intensified. This is the reason why $MgAl_2O_4$ was formed at lower temperatures (1100° C) in the presence of fluorine ions. The F^- ion shows a positive effect on the development of solid-state reactions in which Al_2O_3 is one of the reactants only up to a concentration range in which a substitutional solid solution (in anion sublattice) is formed. With a further increase of AlF_3 concentration, MgF_2, formed as found by X-ray analysis, is what brings about the decreasing of the reaction product amount. The conclusion is supported by the data given in Fig. 1, as well as by the results

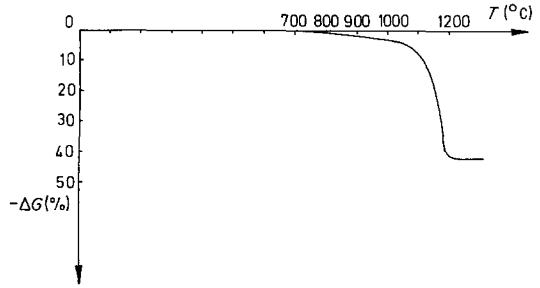

Figure 3 TG curve for pure AlF_3.

TABLE III The influence of AlF_3 on reaction degree in the systems Al_2O_3–γ_2O_3, Al_2O_3–Dy_2O_3, Al_2O_3–SiO_2

Reactants	Temperature, T (° C)	Reaction product	Reaction degree (%)
$2\gamma_2O_3 + 5Al_2O_3$	1200	$3\gamma_2O_3 \cdot 5Al_2O_3$	10
$3\gamma_2O_3 \cdot 5Al_2O_3 + 1.5AlF_3$	1200	$3\gamma_2O_3 \cdot 5Al_2O_3$	20
$3Dy_2O_3 + 5Al_2O_3$	1300	$3Dy_2O_3 \cdot 5Al_2O_3$	26
$3Dy_2O_3 + 5Al_2O_3 + 1.5\%AlF_3$	1300	$3Dy_2O_3 \cdot 5Al_2O_3$	70
$2SiO_2 + 3Al_2O_3$	1500	$2SiO_2 \cdot 3Al_2O_3$	45
$2SiO_2 + 3Al_2O_3 + 1.5\%AlF_3$	1500	$2SiO_2 \cdot 3Al_2O_3$	67

of spinel synthesis in pure Al_2O_3–MgO samples packed in loose AlF_3 and CaF_2 powders.

$\gamma \rightarrow \alpha$ transition in Al_2O_3 took place at 140° C lower temperature in the presence of F^- ion (Fig. 2), which is the consequence of the increased cation vacancy concentration. The increased cation vacancy concentration in Al_2O_3 due to F^- ion presence must cause the decrease of anion vacancy concentration in the bulk. Bearing in mind the densification mechanism of Al_2O_3 [3], the presence of AlF_3 should retard shrinkage during sintering. The data in Fig. 4 prove that in the presence of AlF_3 (curve I) the densification during sintering is remarkably slower.

Besides the decrease of anion vacancy concentration in the bulk the retardation of densification is caused by the change of surface properties of Al_2O_3 powder particles, due to presence of fluorine ion. Specific surface area change of Al_2O_3 powder with increasing temperature is given in Fig. 5. The drop of the measured specific surface area values, as well as the change of the particle shape (Fig. 6), which influence mass transport during sintering, are the consequence of the intensified surface diffusion at lower temperatures (below 1000° C) in the presence of F^-. The intensified surface diffusion due to adsorption of negative fluorine ion in the Al_2O_3 surface can be explained on the basis of Kröger's theory of surface diffusion [4].

The beneficial influence of F^- ion on the synthesis of $MgAl_2O_4$ starting with Al_2O_3 and MgO, is a consequence of the cation vacancy concentration increase in the reaction system. Due to the incorporation of F^- in the O^{2-} lattice sites, the cation diffusion intensifies enabling $MgAl_2O_4$ formation at much lower temperatures, compared with the systems not containing F^- ions.

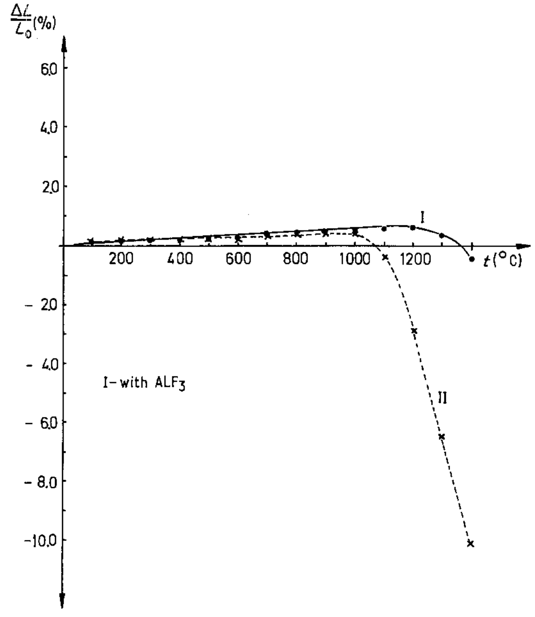

Figure 4 Shrinkage data for Al_2O_3 with and without AlF_3.

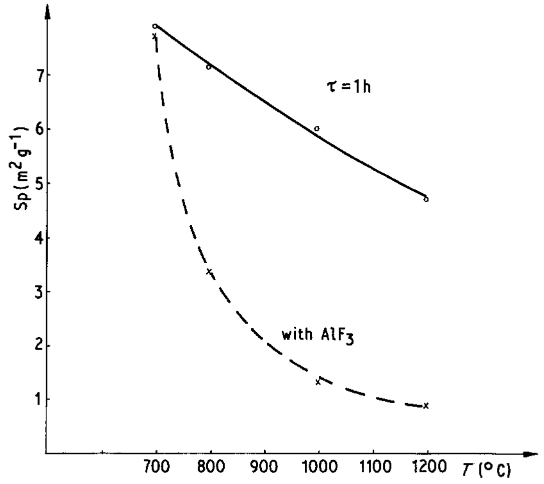

Figure 5 Specific surface area change as a function of temperature for Al_2O_3 powder with and without AlF_3.

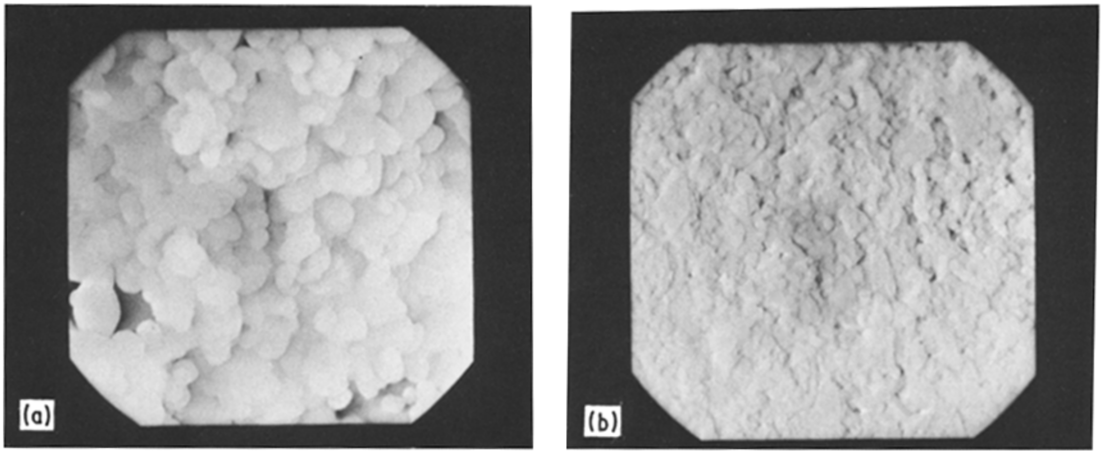

Figure 6 SEM of Al_2O_3 particles with (a) and without (b) AlF_3 at 1200° C and 1 h (× 10 000).

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