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EFFECTS OF FLUORIDE ADDITIVES, LiF, NaF AND CaF_2, ON THE SOLID-STATE REACTIONS IN THE $MgO-Cr_2O_3$ AND $ZnO-Cr_2O_3$ SYSTEMS

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Interesting effects of fluoride additives, LiF, NaF and CaF_2, on the solid-state reactions in the $MgO - Cr_2O_3$ and $ZnO - Cr_2O_3$ systems under an atmosphere of nitrogen were observed by means of DTA. For the $MgO - Cr_2O_3 - MF$ ($M =$ Li, Na) systems, it was concluded that the melting of the fluoride additives plays an important role in accelerating the second reaction step at around 1000°. On the other hand, for the $ZnO - Cr_2O_3 - MF$ ($M =$ Li, Na) systems, a great acceleration by the additives was observed in the first reaction step at around 700°, a much lower temperature than the melting points of the fluorides. The effect of CaF_2 was not clear in either system.

In a previous paper [1], the solid-state reactions in the $MgO-Cr_2O_3$ and $ZnO-Cr_2O_3$ systems under atmospheres of oxygen, air or nitrogen were investigated by means of DTA and isothermal kinetic techniques.

For the $MgO-Cr_2O_3$ system, it was considered that the reaction proceeds through the following steps: (1) Initial reaction step (exothermic DTA peak at around 800°): oxidation of Cr_2O_3 with oxygen in the atmosphere to CrO_3 under the catalytic action of MgO, followed by the coverage of the MgO grains with CrO_3 formed and formation of a thin layer of spinel on the surface of the MgO grains, $MgO + 2\,CrO_3 \rightarrow MgCr_2O_4 + 3/2\,O_2$. (2) second reaction step (exothermic DTA peak at around 1000°): growing of the product layer inwards into the grains of MgO, Cr_2O_3 being transported by diffusion of chromium ions through this layer to the MgO/spinel interface at which the reaction proceeds. The DTA peak corresponding to this second step appeared only in the nitrogen atmosphere.

For the $ZnO-Cr_2O_3$ system, the initial reaction step (exothermic DTA peak at around 700 – 800°) proceeds under the catalytic action of ZnO in a similar manner as that in the $MgO-Cr_2O_3$ system, but it was considered that the catalytic mechanism for ZnO differs from that for MgO. Although these catalytic mechanisms are not clear, it was speculated that the active oxygen adsorbed on the surface of the MgO, and the oxygen ions in the ZnO lattice, play important roles in the oxidation of Cr_2O_3 to CrO_3 in the initial step. The second reaction step (exothermic peak at about 1100°) proceeds at the same temperature regardless of the atmosphere.

The present paper is concerned with a thermoanalytical study on the effects of fluoride additives, LiF, NaF and CaF_2, on the solid-state reactions in the $MgO-Cr_2O_3$ and $ZnO-Cr_2O_3$ systems under an atmosphere of nitrogen.

The authors have already reported on the effects of halide additives on the formation of $MgAl_2O_4$ [2, 3] and $MgFe_2O_4$ [4] by means of both thermoanalytical and isothermal kinetic tehniques. These experiments suggested that the reactions between the fluoride and reactants promote spinel formation in the initial reaction step, and that compounds produced by the initial reaction accelerate diffusion in the second reaction step. In addition, it was found that the cations of the fluorides play an important role in accelerating diffusion in the second reaction step; for the $MgO-Al_2O_3$ system the promoting actions are in the order $LiF \geq NaF > > BaF_2 > MgF_2 > CaF_2$.

Experimental

In general, experiments were carried out in accordance with the methods given previously [1].

Materials

MgO, ZnO and Cr_2O_3 were prepared by the same methods as in [1]; the mean particle size was 0.1, 0.5 and 0.5, 1.0 μm, respectively. LiF (Wako), NaF and CaF_2 (Kanto) additives were reagent grade materials, and were used without further purification.

Preparation of samples

Equimolar mixtures of the oxide powders, $MgO-Cr_2O_3$ and $ZnO-Cr_2O_3$, were blended with additives (10 mole%) for 60 min in an agate mortar. Powder mixtures were used in DTA experiments, but in isothermal kinetic experiments pellet samples prepared by pressing the mixtures under a pressure of 150 kg/cm^2 and broken into five pieces were used.

Chemical analysis

The fractional formations of $MgCr_2O_4$ and $ZnCr_2O_4$ for the systems with LiF and NaF additives were determined by estimating the unreacted MgO and ZnO, respectively. For the CaF_2 additive systems X-ray analysis was used.

Thermal analysis

DTA experiments were carried out with a Thermoflex 8001 apparatus (Rigaku Denki) under an atmosphere of nitrogen (300 mm Hg). Pt–Pt/13 Rh thermocouples and a heating rate of 10°/min were used. X-ray analysis of the samples at various temperatures in the DTA experiments (shown by arrows) was carried out to study the reaction mechanisms involved.

X-ray diffraction

The diffractometer used was of Geigerflex 2001 type (Rigaku Denki) and was operated under the following conditions: Cu target, Ni filter, 25 kV and 10 mA.

Isothermal kinetic experiments

Compact pellets were placed in a Pt boat (10×45×15 mm) and heated in an isothermally-operated furnace. An experimental atmosphere of nitrogen (300 mm Hg) was used. The apparatus was first evacuated to approximately $10^{-2} \sim 10^{-3}$ mm Hg and then filled with nitrogen of the prescribed pressure.

Results and discussion

$MgO-Cr_2O_3$ and $MgO-Cr_2O_3-MF(MF_2)$ systems

Figure 1 shows the DTA curves for the $MgO-Cr_2O_3$ and $MgO-Cr_2O_3-MF(MF_2)$ systems in a N_2 atmosphere (300 mm Hg). X-ray analysis was carried out on samples cooled from the temperatures indicated by the arrows. Some of the results are shown in Figs 2(a) and 3. Count-full scales are 800 counts/sec in Figs 2 and 3(d), and 2000 counts/sec in Figs 3(b) and (c).

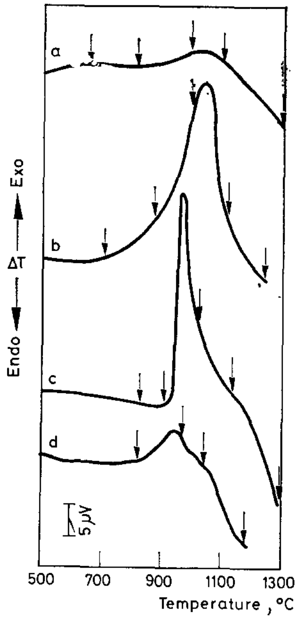

Fig. 1. DTA curves for the $MgO-Cr_2O_3$ and $MgO-Cr_2O_3-MF(MF_2)$ systems in an atmosphere of nitrogen (300 mm Hg). Additives (10 mole%): (a) none; (b) LiF; (c) NaF; (d) CaF_2

Figure 1(a) is the curve for the $MgO-Cr_2O_3$ system without additive, which has already been reported [1]. The broad exothermic peak at about 1020° is due to the formation of $MgCr_2O_4$, which obeys Jander's equation based on diffusion through the product layer. Fractional formation of $MgCr_2O_4$ at 990° was about 12%, but no $MgCr_2O_4$ is identified at 990° in the X-ray diffraction pattern in Fig. 2(a), and even at 1300° certain amounts of the reactants, MgO and Cr_2O_3, remain unreacted.

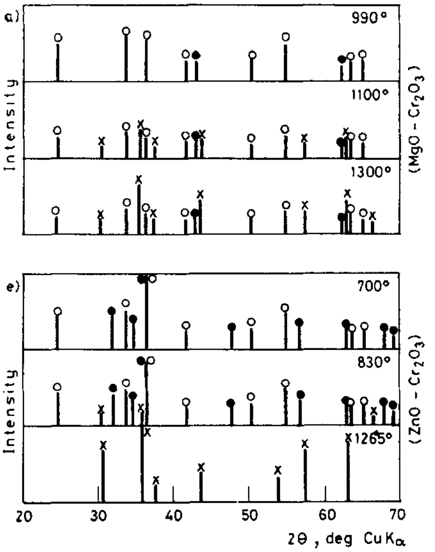

Fig. 2. X-ray diffraction patterns of the samples at various temperatures shown by the arrows in the DTA curves for the $MgO-Cr_2O_3$ (Fig. 1 (a)) and $ZnO-Cr_2O_3$ (Fig. 6(e)) systems. (a) $MgO-Cr_2O_3$; (e) $ZnO-Cr_2O_3$ o Cr_2O_3; ● MgO or ZnO; × $MgCr_2O_4$ or $ZnCr_2O_4$

Figures 1(b) and (c) are the DTA curves for the $MgO-Cr_2O_3-LiF$ and $MgO-Cr_2O_3-NaF$ systems, respectively. The exothermic peaks are large and sharp compared with curve (a); especially curve (c) tends to be explosive, but each peak temperature (1030° and 960°) is approximately the same as in curve (a). X-ray diffraction patterns for the samples at 990° in curve (b) and 1020° in (c) show $MgCr_2O_4$ alone. This means that the LiF or NaF additive greatly promotes the rate of the solid-state reaction in the $MgO-Cr_2O_3$ system.

Curve (d) is for the $MgO-Cr_2O_3-CaF_2$ system. From the size of the exothermic peak and X-ray diffraction patterns (Fig. 3(d)), it is concluded that the promoting action of CaF_2 is observed, but is smaller than in (b) and (c).

Figure 4 shows the DTA curves for the Cr_2O_3-MF (1 : 1 mole), $MgO-MF$ (1 : 1 mole) and $ZnO-MF$ (1 : 0.1 mole) systems, where M is Li or Na. Endothermic peaks in the DTA curves correspond to the melting of the systems. Melting points of 800, 820, 825, 920, 940 and 945°, which are somewhat lower than that of the additive alone, were found for the Cr_2O_3–LiF (b-1), MgO–LiF (b-2), ZnO–LiF (f-1), Cr_2O_3–NaF (c-1), MgO–NaF (c-2) and ZnO–NaF (g-1) systems, respectively. These melting points were estimated from the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the endothermic peak with the extrapolated base line. No thermal change in the DTA curves can be observed except for the melting, and no difference in the X-ray

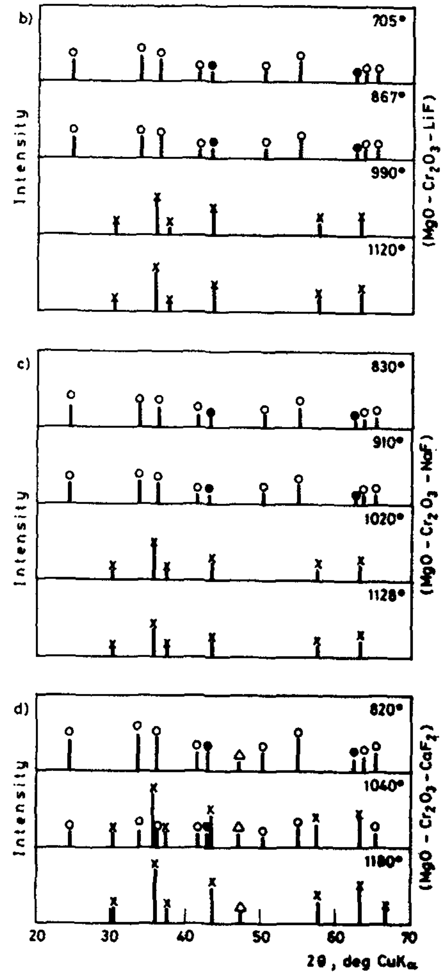

Fig. 3. X-ray diffraction patterns of the samples at various temperatures shown by the arrows in the DTA curves for the $MgO-Cr_2O_3-MF(MF_2)$ systems in Fig. 1. Additives: (b) LiF; (c) NaF; (d) CaF_2; ○ Cr_2O_3; ● MgO; × $MgCr_2O_4$; △ CaF_2

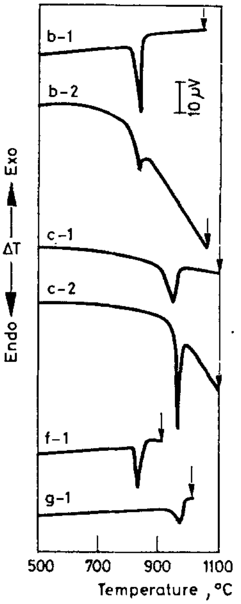

Fig. 4. DTA curves for the Cr_2O_3–MF (1 : 1), MgO–MF (1 : 1) and ZnO–MF (1 : 0.1) systems in an atmosphere of nitrogen (300 mm Hg). (b–1) Cr_2O_3–LiF; (b–2) MgO–LiF; (c–1) Cr_2O_3–NaF; (c–2) MgO–NaF; (f–1) ZnO–LiF; (g–1) ZnO–NaF

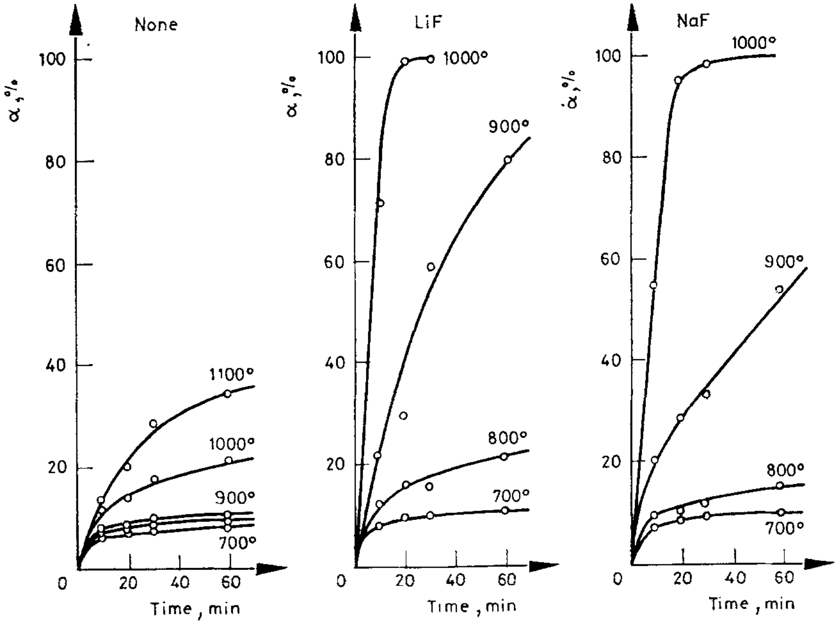

Fig.5. Fractional conversion (α) as a function of time at various temperatures in an atmosphere of flowing nitrogen (50 ml/min) for the MgO–Cr_2O_3 system, and of static nitrogen (300 mm Hg) for the MgO–Cr_2O_3–MF (M = Li, Na) systems

diffraction patterns of the samples before and after (indicated by arrows) the experiments can be detected.

The steep rises of the DTA curves in Figs 1(b) and 1(c) appear at temperatures just after these melting points. This shows that in the system with the additive melting occurs first, followed by rapid reaction. On the other hand, for the system with the CaF_2 additive the melting of CaF_2 was not observed in the temperature range of the DTA experiment. From these results, in the $MgO-Cr_2O_3-MF$ systems under a N_2 atmosphere, it is concluded that the melting of the fluoride additives plays an important role in accelerating the second reaction step.

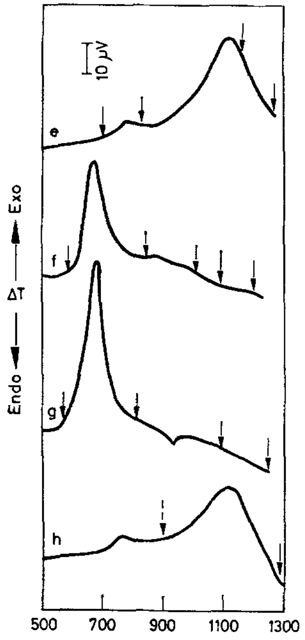

Fig. 6. DTA curves for the $ZnO-Cr_2O_3$ and $ZnO-Cr_2O_3-MF(MF_2)$ systems in an atmosphere of nitrogen (300 mm Hg). Additives (10 mole %): (e) none; (f) LiF; (g) NaF; (h) CaF_2

The isothermal kinetic experiments on the formation of $MgCr_2O_4$ in the $MgO-Cr_2O_3-MF$ (M = Li, Na) systems in a nitrogen atmosphere were carried out in the range 700 ~ 1000°, and compared with the results of the DTA experiments described above. As shown in Fig. 5, the reaction in the systems with additive proceeds much more rapidly than without additive, especially above the melting temperature of the additive systems. The data at 700 and 800° could fit Jander's equation, but the data at 900° not. This is probably because the reaction proceeds in the molten state at 900°. X-ray analysis at room temperature of the samples formed during the reactions did not reveal any intermediate formed with the additives.

$ZnO-Cr_2O_3$ and $ZnO-Cr_2O_3-MF(MF_2)$ systems

Figure 6 shows the DTA curves for the $ZnO-Cr_2O_3$ anc $ZnO-Cr_2O_3-MF(MF_2)$ systems in a N_2 atmosphere (300 mm Hg). Compared with the $MgO-Cr_2O_3$ systems, a marked difference in their response to the additives can be detected in the DTA curves. X-ray analysis was carried out on samples at the temperatures indicated by the arrows. Some of the results are shown in Figs 2(e) and 7. The count-full scale in Fig. 7 is 800 counts/sec.

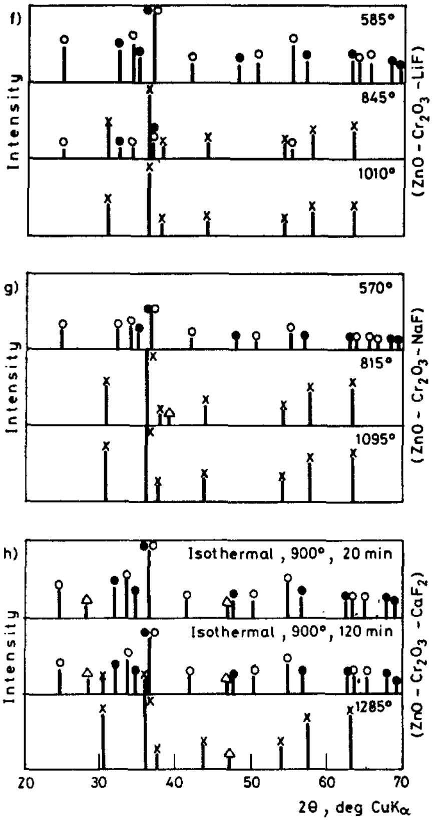

Fig. 7. X-ray diffraction patterns of the samples at various temperatures shown by the arrows in the DTA curves for the $ZnO-Cr_2O_3-MF(MF_2)$ systems in Fig. 6. Additives: (f) LiF; (g) NaF; (h) CaF_2; ○ Cr_2O_3; ● ZnO; × $ZnCr_2O_4$; △ NaF or CaF_2

Figure 6(e) is the curve for the $ZnO-Cr_2O_3$ system without additive [1]. The first, small exothermic peak appears at 780°, followed by the second, large exothermic peak at 1120°. These peaks are due to the formation of $ZnCr_2O_4$. The fractional formations of $ZnCr_2O_4$ were 12.5% at 830° and 100% at 1265°. The X-ray diffraction pattern at 830° shows the formation of small amounts of $ZnCr_2O_4$ (Fig. 2(e)).

Figure 6(f) is the DTA curve for the $ZnO-Cr_2O_3-LiF$ system. The large exothermic peak at 1120° in curve (e) is seen to be greatly shifted to 670°, the temperature region of the first reaction step in curve (e). On the basis of X-ray analysis of the samples (585 and 845°) before and after this peak, it can be concluded that this peak at 670° is due to the formation of $ZnCr_2O_4$. A small endothermic peak at about 850° may be due to the melting of this system, because this peak corresponds to the DTA endothermic peak due to the melting of the $ZnO-LiF$ and Cr_2O_3-LiF systems (Fig. 4). Therefore, it is found that the promoting action of the LiF additive on the reaction occurs before the melting temperature. Curve (g) is the DTA curve for the $ZnO-Cr_2O_3-NaF$ system, and is analogous to curve (f). X-ray diffraction patterns of the samples before and after the large exothermic peak at 680° are shown in Fig. 7(g). From a consideration of the results of curves (c-1) and (g-1) in Fig. 4, the small endothermic peak at about 940° is also due to the melting of this system. Although these interesting promoting mechanisms in the $ZnO-Cr_2O_3-MF$ systems are not clear in detail, it is speculated that a pronounced distortion of the ZnO lattice by the MF additives plays an important role in the reacting state.

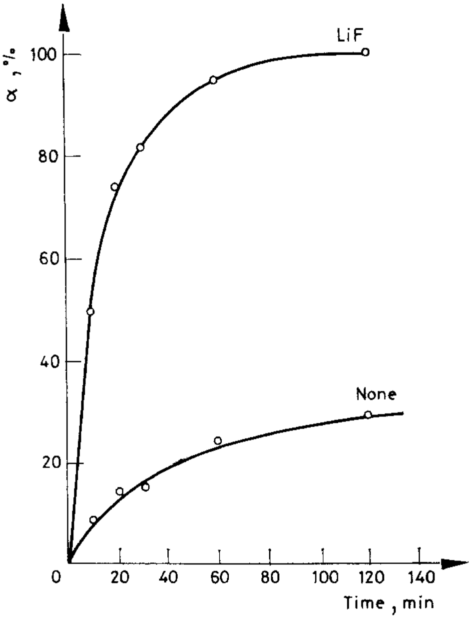

Fig. 8. Fractional conversion (α) as a function of time at 900° in an atmosphere of nitrogen (300 mm Hg) for the $ZnO-Cr_2O_3$ and $ZnO-Cr_2O_3-LiF$ systems

Figure 6(h) is the DTA curve for the $ZnO-Cr_2O_3-CaF_2$ system. No promoting action of the CaF_2 additive can be detected, because the shape of curve (h) is analogous to that of curve (e). X-ray diffraction patterns at 900° and 1285° are shown in Fig. 7(h). The results at 900° were obtained not on the DTA samples, but on the samples produced in the isothermal experiments for 20 and 120 min at 900°. Only a small amount of $ZnCr_2O_4$ is detected after 120 min at 900°. This means that the effect of the cation of the fluoride on the promotion of the reaction is also an important factor.

Figure 8 shows the results of isothermal kinetic experiments on the formations of $ZnCr_2O_4$ for the $ZnO-Cr_2O_3$ and $ZnO-Cr_2O_3-LiF$ systems in a N_2 atmosphere (300 mm Hg) at 900°. The promoting effect of the LiF additive is clearly shown.

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Résumé — On a étudié par ATD les effets intéressants des fluorures LiF, NaF et CaF_2 utilisés comme additifs sur les réactions en phase solide des systèmes $MgO-Cr_2O_3$ et $ZnO-Cr_2O_3$ en atmosphère d'azote. Pour les systèmes $MgO-Cr_2O_3-MF$ (M = Li, Na), on conclut que la fusion des fluorures joue un rôle important sur l'accélération de la seconde étape de réaction, à 1000° environ. D'autre part, pour les systèmes $ZnO-Cr_2O_3-MF$ (M = Li, Na) on a observé l'effet de grande accélération dû aux additifs lors de la première étape de réaction, à 700° environ, température bien inférieure à celle de la fusion des fluorures. L'effet de CaF_2 n'est pas encore clair pour chacun des deux systèmes.

Zusammenfassung — Die interessanten Effekte der Fluoridadditive LiF, NaF und CaF_2 und die Festphasenreaktionen in $MgO-Cr_2O_3$ und $ZnO-Cr_2O_3$ Systemen in Stickstoffatmospäre wurden durch die DTA-Technik beobachtet. Für die Systeme $MgO-Cr_2O_3-MF$ (M = Li, Na) wurde gefolgert, daß das Schmelzen der Flouridadditive eine wichtige Rolle bei der Beschleunigung der zweiten Reaktionsstufe bei etwa 1000° spielt. Andererseits wurde für die Systeme $ZnO-Cr_2O_3-MF$ (M = Li, Na) die grosse Beschleunigung durch Additive in der ersten Reaktionsstufe bei ungefähr 700° beobachtet, also bei viel niedrigeren Temperaturen als das Schmelzen der Fluoride. Die Wirkung von CaF_2 war für keines der beiden Systeme eindeutig.

Резюме — С помощью ДТА наблюдали интересные влияния таких фторидных добавок, как LiF, NaF и CaF_2 на твердотельные реакции в системах $MgO-Cr_2O_3$ и $ZnO-Cr_2O_3$ в атмосфере азота. Для систем $MgO-Cr_2O_3-MF$ (M = Li, Na) был сделан вывод, что плавление фторидных добавок играет вамную роль в ускорении второй реакционной стадии около 1000°. С другой стороны, для систем $ZnO-Cr_2O_3-MF$ (M = Li, Na), большое ускорение добавками наблюдалось в первой реакционной стадии около 700° т. е. при намного более низкой температуре, чем плавление фторидов. Влияние CaF_2 в обоих системах не было ясным.