

THERMOANALYTICAL STUDY OF THE SOLID-STATE REACTIONS IN MgO-Cr₂O₃ AND ZnO-Cr₂O₃ SYSTEMS

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The solid-state reactions in MgO-Cr₂O₃ and ZnO-Cr₂O₃ systems under atmospheres of oxygen, air and nitrogen were investigated by means of DTA and isothermal kinetic techniques. It was shown that the application of DTA to the solid-state reactions affords useful information with respect to the initial reaction stage: oxidation of Cr₂O₃ to CrO₃ in the presence of MgO or ZnO, followed by the formation of a thin layer of spinel, which consisted of an imperfect lattice, on the surface of the MgO or ZnO grains.

One of the interesting applications of thermal analysis is for the investigation of reactions in mixtures of solids. The isothermal kinetic techniques have made many important contributions to kinetic studies, but these are time-consuming for the study of solid-state reactions over a wide temperature range. Furthermore, a difficulty arises in clarifying the reaction process in the initial reaction stage before a fixed reaction temperature is reached, because a higher temperature is generally applied to the reaction of solids.

Differential thermal analysis (DTA) is a non-isothermal technique which differs essentially from such a conventional isothermal method. A striking advantage of DTA tests is that the procedure requires only a small fraction of the time, and reaction processes over wide temperature ranges can be followed directly by observation of the DTA curve. Therefore, it can be expected that the results obtained from the DTA technique will provide new information which could not be obtained from the conventional isothermal techniques. Although considerable importance and interest have been attached to the study of reaction kinetics by DTA, the quantitative analysis of DTA curves is very complex because it is a dynamic investigation method. In order to understand completely the physical or chemical meaning of thermal deflections in DTA curves, other techniques such as X-ray diffraction, chemical analysis, gas analysis, etc. must also be used in conjunction with the DTA study.

In our laboratory DTA techniques have been applied extensively to study the reaction processes of various types of chemical reactions. The present paper involves the application of both DTA and isothermal kinetics to studies of the solid-state reactions in MgO-Cr₂O₃ and ZnO-Cr₂O₃ systems.

Many studies have been made on the MgO-Cr₂O₃ system by means of isothermal kinetics, but the mechanism of the formation of chromite is still not fully understood. Literature surveys relating to the kinetic analysis of solid-state reactions in the MgO-Cr₂O₃ system have been made by Hulbert et al. [1] and Haber et al. [2]. On the other hand, few papers can be obtained relating to kinetic studies on ZnO-Cr₂O₃ [3].

Experimental

Materials

MgO and Cr₂O₃ were prepared by calcining commercial Mg(OH)₂ and Cr₂O₃ (reagent grade, Kanto Chemical Co.) at 1300° for 2 hr in air. ZnO was prepared by calcining commercial ZnO (reagent grade, Kanto) at 500° for 2 hr in air. The mean particle size was estimated with the aid of an electron microscope: MgO: 0.1 μm, ZnO: 0.5 μm and Cr₂O₃: 0.5-1.0 μm. The BET surface areas of MgO, ZnO and Cr₂O₃ were 25.0, 14.7 and 3.8 m²/g, respectively.

Preparation of samples

Equimolar mixtures of the oxide powders MgO-Cr₂O₃ and ZnO-Cr₂O₃ were prepared by blending for 40 min in an agate mortar. Pellets (*d* = 2 cm) were formed by pressing the mixtures under a pressure of 150 kg/cm², and broken into five pieces as the reacting samples.

Chemical analysis

The fractional formations of MgCr₂O₄ and ZnCr₂O₄ were determined by estimating the unreacted MgO and ZnO, respectively. 2M HCl solution (10 ml) was added to the reacted sample (100 mg) and made up to 100 ml with distilled water. The mixture was boiled for 30 min, allowed to cool and filtered, and the filtrate was titrated with EDTA solution.

The amount of Cr⁶⁺ ion in the sample was determined by the diphenylcarbazide method. The sample (100 mg) was treated with 2M H₂SO₄ (10 ml), boiled and filtered. One ml of 0.25% diphenylcarbazide in acetone was added to the filtrate, which was then diluted to 100 ml with distilled water. The amount of chromate ions was determined photocolometrically (Hitachi 101 photometer, wavelength 540 μm).

X-ray diffraction analysis

The phase compositions of the samples were determined by means of the X-ray powder method, using a diffractometer (Rigaku Denki, Geigerflex 2141). CuKα radiation was employed with a Ni filter.

Thermal analysis

DTA experiments were carried out with a Thermoflex 8001 apparatus (Rigaku Denki). Pt-Pt/13Rh thermocouples were used for measuring the temperature. A heating rate of 10°/min was employed in all experiments. The sample weight was 600–800 mg. α -Al₂O₃ was taken as standard material. Three experimental atmospheres of air (1 atm), O₂ (10–600 mm Hg) and N₂ (10–600 mm Hg) were used. In the cases of oxygen and nitrogen atmospheres, the apparatus was first evacuated to approximately 10⁻¹ mm Hg and then filled with oxygen or nitrogen of the prescribed pressure.

Isothermal kinetic experiments

Compact pellets were placed in a Pt boat (10 × 45 × 15 mm) and heated in the isothermally-operated furnace. The three atmospheres of oxygen, air and nitrogen were used at a flow rate of 50 ml/min.

Results and discussion

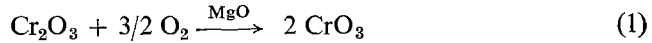
MgO-Cr₂O₃ system

Figure 1 shows the DTA curves in atmospheres of oxygen (300 mm Hg), air (1 atm) and nitrogen (300 mm Hg), and the fractional conversions (α) and Cr⁶⁺ contents of the samples at various temperatures shown by arrows on the DTA curves. A broad exothermic peak appears in the range 700–950° in the presence of oxygen, while in the nitrogen atmosphere it appears at above 850°. X-ray diffraction patterns of the samples obtained at temperatures before and after the exothermic peak show that the peak corresponds to the formation of MgCr₂O₄. No evidence of formation and decomposition of any intermediate chromate phase during the course of the reaction was shown by means of X-ray analysis. The changing behaviours of α correspond well to the DTA curves. In oxygen and air atmospheres, the Cr⁶⁺ content changes with an opposite tendency to that of α , while in nitrogen it is virtually invariant.

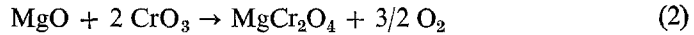
On the other hand, in the DTA analysis of the initial Cr₂O₃ sample (Cr⁶⁺ = 0.08 mg/g sample) in the range 300–1300° under oxygen, air and nitrogen atmospheres, no thermal change appeared and the Cr⁶⁺ contents in the samples at various temperatures on the DTA curves were approximately the same as the initial one. These observations make it necessary to consider the catalytic effect of MgO on the oxidation of Cr₂O₃ to CrO₃ in the initial reaction stage of the MgO-Cr₂O₃ binary system.

On the basis of these thermoanalytical data it can be presumed that the mechanism of the solid-state reaction in the powdered mixture of MgO and Cr₂O₃ under the atmospheres containing oxygen proceeds through the following steps:

a) Oxidation of Cr₂O₃ to CrO₃ in the presence of MgO:



b) Coverage of MgO grains with chromium oxide by means of a transport reaction and/or surface diffusion, and formation of a thin layer of spinel on the surface of the MgO grains:



If the MgO samples are regarded as spherical in shape and 0.1 μm in diameter, and the fractional conversion is 50%, the formation of a thin spinel layer of about

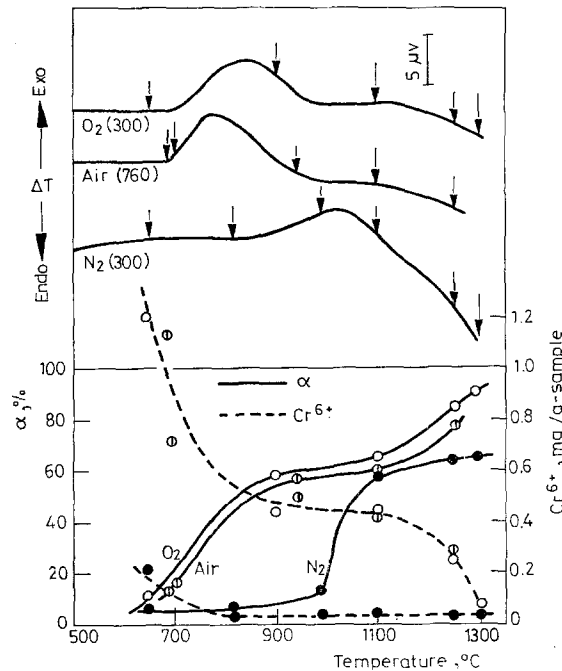


Fig. 1. DTA curves in atmospheres of oxygen (300 mm Hg), air (1 atm) and nitrogen (300 mm Hg) for the MgO—Cr₂O₃ system, and the fractional conversion (α) and Cr⁶⁺ content of the samples at various temperatures on the DTA curves

100 Å is evaluated. The initial reaction step is followed by decreases in the fresh surface of the MgO grains, in the catalytic effect of MgO for the oxidation of Cr₂O₃, and in the Cr⁶⁺ content remaining in the sample.

c) Growing of the product layer inwards into the grains of MgO, Cr₂O₃ being transported by diffusion of chromium ions through this layer to the MgO/spinel interface at which the reaction proceeds. In this third step the reaction rate is

determined by the rate of diffusion of chromium ions through the spinel. The DTA peak in the nitrogen atmosphere corresponds to this third reaction step.

The isothermal kinetic experiments on the formation of MgCr_2O_4 in the $\text{MgO}-\text{Cr}_2\text{O}_3$ system in oxygen, air and nitrogen atmospheres were carried out in the range $700-1000^\circ$, and compared with the results of the DTA experiments de-

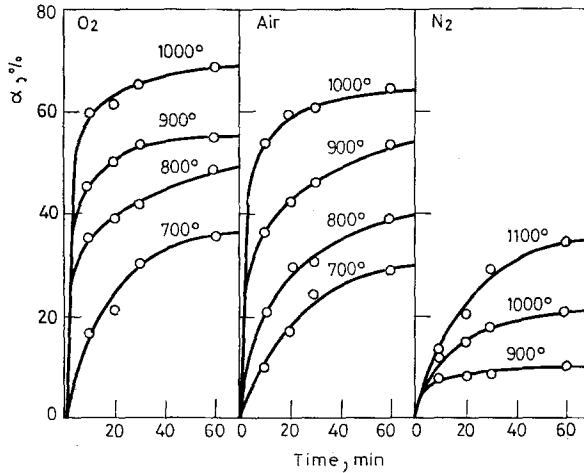


Fig. 2. Fractional conversion (α) as a function of time at various temperatures in flowing atmospheres (50 ml/min) of oxygen, air and nitrogen for the $\text{MgO}-\text{Cr}_2\text{O}_3$ system

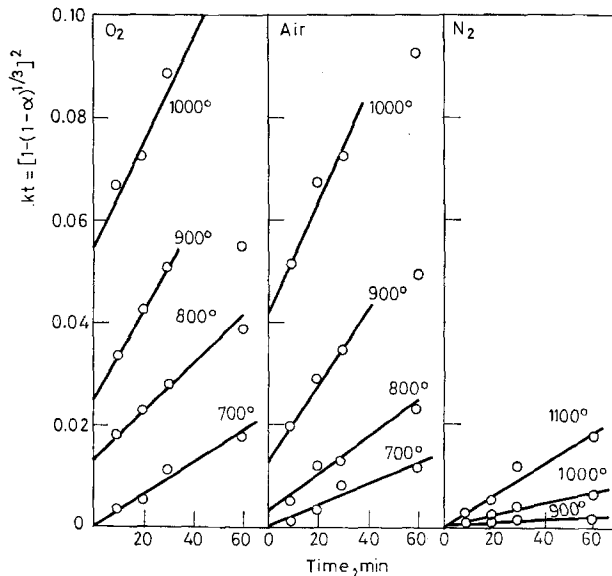


Fig. 3. Jander's plots for the $\text{MgO}-\text{Cr}_2\text{O}_3$ system

scribed above. As shown in Fig. 2, the reaction in oxygen and air atmospheres proceeds much more rapidly than in a nitrogen atmosphere, and a higher degree of conversion is attained within a short period of time (about 10 min).

Figure 3 shows the results plotted according to Jander's equation based on diffusion through the reaction product layer. It can be seen that the data can fit Jander's equation, but the lines above 800° for the experiments in the presence of oxygen do not pass through the origin. All of the data for reaction times above 60 min deviate greatly from these lines. The lines for oxygen and air atmospheres intersect the ordinate at kt values corresponding to $\alpha = 10-55\%$, whereas for a nitrogen atmosphere the lines pass through the origin. The results in oxygen and air atmospheres show that in the initial reaction stage the rapid chemical reaction promoted by oxygen in the atmospheres takes place, and then the reaction controlled by diffusion through this layer proceeds. From comparison of the DTA and isothermal kinetic results, it is also considered that the bulk of the DTA exothermic peak in the range $700-950^\circ$ corresponds to the initial reaction promoted by oxygen in the atmospheres.

The activation energies (E) estimated were 11.5, 14.5 and 30.5 Kcal/mole in oxygen, air and nitrogen atmospheres, respectively. The values of E in oxygen and air atmospheres are very small compared with that of the solid-state reactions usually. These data imply that the thin layer formed in the initial stage consists of an imperfect lattice. The imperfections in the lattice make possible rapid diffusion of chromic oxide species through the product layer, and thus a high reaction rate. As the reaction proceeds, however, the product phase becomes more and more ordered, causing a continuous decrease in the diffusion rate. The different behaviours in oxygen and nitrogen atmospheres can be understood through the reaction mechanisms considered above.

ZnO-Cr₂O₃ system

Figure 4 shows the DTA curves in atmospheres of oxygen (600, 300, 150 and 10 mm Hg), air (1 atm) and nitrogen (600, 300 and 10 mm Hg), and the fractional conversions and Cr^{6+} contents of the samples at the temperatures shown by arrows on the DTA curves in atmospheres of oxygen (300 mm Hg), air (1 atm) and nitrogen (300 mm Hg). In all DTA curves, the first, small exothermic peak appears in the range $650-850^\circ$, followed by the second, large exothermic peak in the range $900-1200^\circ$. The first peak shifts to lower temperature and its area increases somewhat as the partial pressure of oxygen in the atmospheres rises. The effect of the atmosphere on the second peak temperature is not clear, but the second peak tends to increase in area as the first peak area decreases. The increase of α corresponds well to the DTA curves. The decreases in the Cr^{6+} contents in the temperature range of the first peak also correspond well to the DTA curves, but in the temperature range of the second peak the Cr^{6+} content remains constant at the initial Cr_2O_3 sample level. A marked difference between the $ZnO-Cr_2O_3$ and $MgO-Cr_2O_3$ systems is that in the former the first peak area, the fractional

conversion and the Cr⁶⁺ content are all small, and the first peak appears even in N₂, while the large second peak appears at the same temperature regardless of the atmosphere.

On the basis of these experimental results, it can be considered with regard to the first peak that a reaction analogous to that in the MgO-Cr₂O₃ system proceeds with the catalytic action of ZnO, but the catalytic mechanism for ZnO

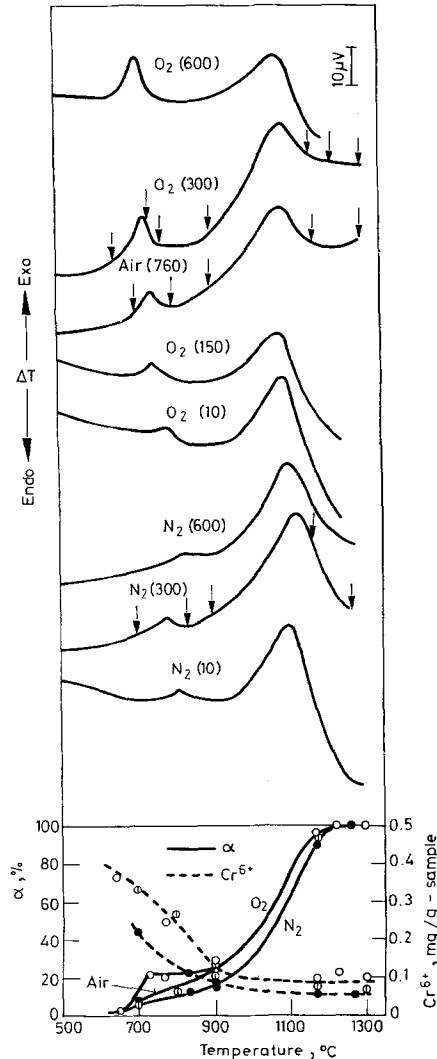


Fig. 4. DTA curves in atmospheres of oxygen (10–600 mm Hg), air (1 atm) and nitrogen (10–600 mm Hg) for the ZnO-Cr₂O₃ system, and the fractional conversion (α) and Cr⁶⁺ content of the samples at the temperatures shown by arrows on the DTA curves

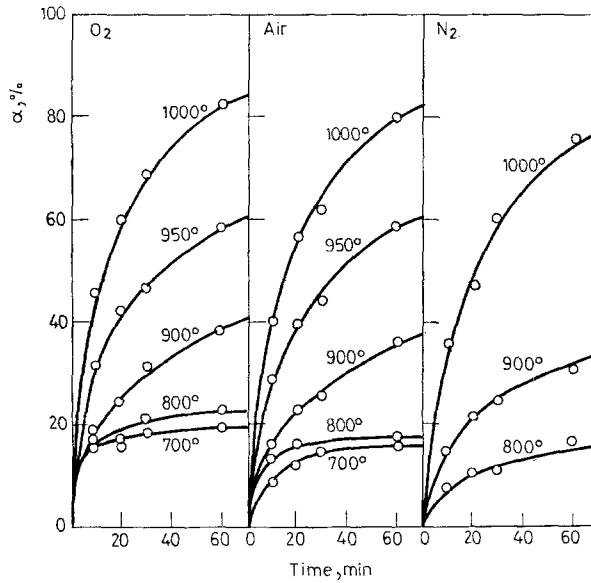


Fig. 5. Fractional conversion (α) as a function of time at various temperatures in flowing atmospheres (50 ml/min) of oxygen, air and nitrogen for the ZnO-Cr₂O₃ system

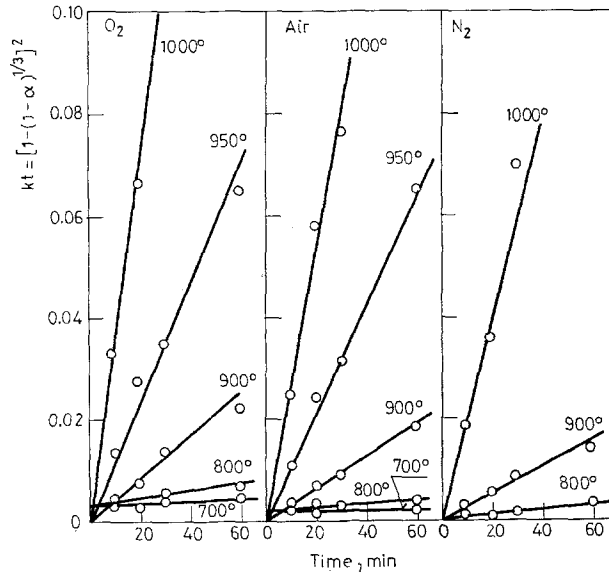


Fig. 6. Jander's plots for the ZnO-Cr₂O₃ system

differs from that for MgO. Although these catalytic mechanisms are not clear in detail, it is speculated that the active oxygen adsorbed on the surface of the MgO, and the oxygen ions in the ZnO lattice, play an important role in the oxidation of Cr₂O₃ to CrO₃ in the ranges 700–950° and 650–850°, respectively.

The isothermal kinetic experiments on the formation of ZnCr₂O₄ in ZnO—Cr₂O₃ systems in flowing oxygen, air and nitrogen atmospheres were carried out in the range 700–1000°, and the results were compared with those of the DTA experiments described above. As shown in Fig. 5, at 700 and 800° in both oxygen and air atmospheres, the reaction proceeds rapidly and attains about 15% conversions within a short period of time (about 10 min), but the reaction then comes to a standstill. In the other cases the reaction seems to proceed continuously.

Figure 6 shows the results plotted according to Jander's equation. It can be seen that the data fit Jander's equation and the reaction controlled by diffusion through the product layer proceeds. However, the data at 700 and 800° for the systems in the presence of oxygen do not pass through the origin, but intersect the ordinate at kt values corresponding to a conversion of about 15%. This shows that in the initial reaction stage the rapid chemical reaction promoted by oxygen occurs within a small conversion range, but in the high temperature range the fraction of the chemical reaction in the initial stage is negligible compared with the total conversion. From a comparison of the DTA and isothermal kinetic results, it is also considered that the bulk of the DTA exothermic peak in the range 650–850° corresponds to the initial reaction promoted by oxygen.

Activation energies estimated from the results in Fig. 6 were 55–65 Kcal/mole in the range 900–1000° for oxygen and air atmospheres and at 800–1000° for nitrogen, whereas at 700–800° for oxygen and air atmospheres activation energies of 13.5 and 15.0 Kcal/mole were found, respectively. In a lower temperature range for oxygen and air atmospheres, the values of E are very small and comparable to that in the initial reaction step of the MgO—Cr₂O₃ system. These data also imply that the thin layer formed in the initial stage is an imperfect lattice. In ZnO—Cr₂O₃ systems, however, in the initial stage α is relatively small in all atmospheres and the greater part of the reaction proceeds according to the diffusion-controlled model.

References

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RÉSUMÉ — Etude des réactions dans l'état solide dans les systèmes MgO—Cr₂O₃ et ZnO—Cr₂O₃ en atmosphères d'oxygène, d'air et d'azote, par ATD et en régime de cinétique isotherme. On montre que l'ATD appliquée aux réactions dans l'état solide fournit des renseignements utiles sur l'étape réactionnelle initiale: l'oxydation de Cr₂O₃ en CrO₃ en présence de MgO ou de ZnO est suivie par la formation d'une couche mince d'une phase spinelle dont le réseau est imparfait, à la surface des grains de MgO ou de ZnO.

ZUSAMMENFASSUNG — Die Festphasenreaktionen in MgO—Cr₂O₃ und ZnO—Cr₂O₃ wurden in Sauerstoff-, Luft- und Stickstoffatmosphäre durch DTA und isotherme kinetische Technik untersucht. Es wurde gezeigt, daß der Einsatz der DTA bei Festphasenreaktionen nützliche Informationen zur Anfangsphase der Reaktion liefert; der Oxidierung von Cr₂O₃ zu CrO₃ folgt, in Gegenwart von MgO oder ZnO, die Bildung einer dünnen Spinellschicht bestehend aus einem unvollständigen Gitter an der Oberfläche von MgO- oder ZnO-Körnchen.

Резюме — С помощью ДТА и изотермической кинетической техники были исследованы реакции в твердом состоянии MgO—Cr₂O₃ и ZnO—Cr₂O₃ в атмосфере кислорода, воздуха и азота. Показано, что применение ДТА при изучении реакций на твердом теле, дает полезную информацию относительно первоначальной реакционной стадии: окисление Cr₂O₃ до CrO₃ в присутствии MgO или ZnO, с последующим образованием тонкого слоя шпинели, которая состоит из несовершенной решетки на поверхности гранул MgO или ZnO.