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MECHANISM OF THE THERMAL DECOMPOSITION OF $3CaO \cdot Al_2O_3 \cdot 6D_2O$

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The mechanism of the step I and step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ was studied. The presence of $Ca(OD)_2$ was proved in the products of the first step of decomposition. In the calorimeter cell of the Dupont 990 thermoanalyser the enthalpy changes $\Delta H_{r,I} = 59.2$ kJ/mole D_2O for step I (210–410°) and $\Delta H_{r,II,1} = 69.0$ kJ/mole D_2O for the first fast part of the step II ("stage 1 of the step II", encompassing the temperature interval 410–560°) were measured. This indicates that the dissociation of $Ca(OD)_2$ is not the only transition taking place in the first fast part (stage 1) of the step II.

The aim of the present study was to achieve, with the aid of thermal methods and X-ray analysis, a quantitative description of reactions ocurring in the course of the thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ at a heating rate of 10° min^{-1}, and thereby contribute to the elucidation of the mechanism of the thermal decomposition of this substance and, consequently, to that of $3CaO \cdot Al_2O_3 \cdot 6H_2O$. Evaluations of the various TG curves differ as regards estimation of the number of decomposition steps of $3CaO \cdot Al_2O_3 \cdot 6H_2O$; e.g. Lefol [1] considers there to be one, Budnikov et al. [2] three, and Govorov [3] four steps.

According to Foreman [4], tricalcium aluminate hexadeuterate $3CaO \cdot Al_2O_3 \cdot 6D_2O$ or $Ca_3Al_2[(OD)_4]_3$ has a structure similar to that of tricalcium aluminate hexahydrate, i.e. it crystallizes in the cubic system and its structure is near to that of grossularite $Ca_3Al_2[SiO_4]_3$.

Experimental

Sample preparation

$3CaO \cdot Al_2O_3 \cdot 6D_2O$ was prepared hydrothermally from $3CaO \cdot Al_2O_3$ during 7 days at 190°. Tricalcium aluminate was prepared by the precursor method by decomposition of organic glass on the basis of calcium and aluminium tartrate. For preparation, heavy water (99.74 mass % D_2O) freed from CO_2 by a 4-hour boiling under reflux was used. In the course of filling and emptying of the autoclave, the temperature of the D_2O never dropped under the boiling point. The product was dried in a stream of water-free nitrogen at 105°. Insufficiently-dried $3CaO \cdot Al_2O_3 \cdot 6D_2O$ reacts even at room temperature with atmospheric carbon dioxide and a phase similar to $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$ is formed.

Methods

Reactions were followed with the TG 951 thermobalance of the Dupont 990 thermoanalyser at a heating rate of 10° min^{-1} in air and stationary nitrogen atmospheres, and with DTA equipment with an adjustable pressure of water vapour, as described by Pach [5]. Some of the samples in various stages of decomposition were investigated by X-ray analysis. The enthalpy changes of the first step (step I, 210–410°) and of the fast first stage (stage 1, 410–560°) of the second step (step II) of the thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ were measured in the calorimeter cell of the Dupont 990 thermoanalyser in a stationary nitrogen atmosphere.

As stage 1 of step II we designated the fast part of the thermal decomposition within the afore-mentioned temperature interval of step II (410–560°). A detailed explanation of the second step of thermal decomposition is given in the discussion.

The enthalpy increase corresponding to step I was determined with the aid of a calorimeter for measuring the heats of solution [6]. The measured heats were then recalculated for one mole D_2O with regard to TG weight losses which correspond to the temperature intervals of the DSC peaks.

Results and discussion

The first step of thermal decomposition

This transition can be described formally, similarly as for $3CaO \cdot Al_2O_3 \cdot 6H_2O$ [7], by the equation:

$$7(3CaO \cdot Al_2O_3 \cdot 6D_2O) = 12\,CaO \cdot 7Al_2O_3 \cdot D_2O + 9\,Ca(OD)_2 + 32\,D_2O$$

TG and DTG curves for $3CaO \cdot Al_2O_3 \cdot 6D_2O$ recorded in an ambient laboratory atmosphere and in a stationary nitrogen atmosphere are given in Fig. 1. The losses of D_2O (in moles) from one mole of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ are listed in Tables 1 and 2. The weight loss after 4 hours heating at 1350° corresponds to 6 moles of D_2O. In the third step of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in a laboratory atmosphere the expression of the weight loss in terms of the number of D_2O moles is just a formal procedure with regard to the dissociation of $CaCO_3$ earlier formed by reaction of CaO with atmospheric CO_2.

The X-ray diagrams show that, after the first step of the thermal decomposition has been completed, a phase similar to that of $12CaO \cdot 7Al_2O_3 \cdot (0-1)H_2O$ prevails. In an analogous way as reported previously [8], among the products of the first step of decomposition the presence of crystals of $Ca(OD)_2$ was proved, from which it follows that $Ca(OD)_2$, apart from being "molecularly" soluble in the transition phase, as assumed by Bartl [9], is also most probably deposited in crystalline form at the grain boundaries of the transition phase. The grain boundaries in the decomposition products are virtually inaccessible for atmospheric CO_2; this was proved in such a way that in the first step of decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in CO_2 atmosphere no formation of $CaCO_3$ was detected.

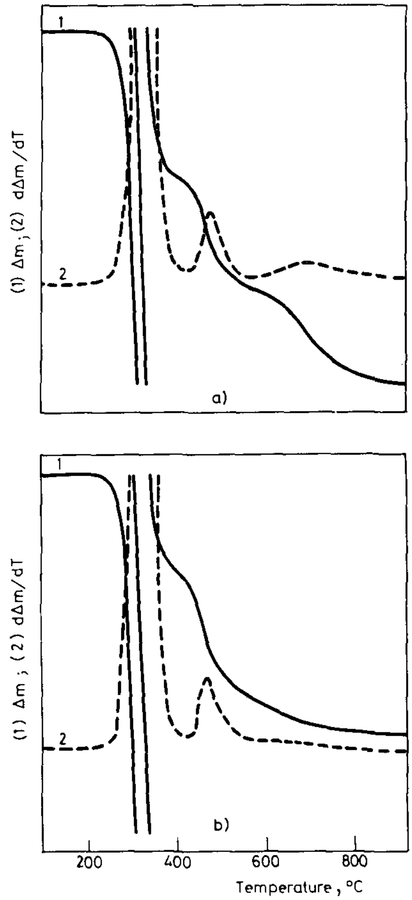

Fig. 1. TG (continuous lines) and DTG (dashed lines) curves of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in a laboratory atmosphere (*a*) and in a stationary nitrogen atmosphere (*b*).

As a test of the reversibility of processes taking place in step I of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$, the products of step I of decomposition of this substance in a D_2O vapour atmosphere at 136° and about 20 kPa were heated. The phase composition of the sample remained unchanged. Since the physical or chemical sorption of water was proved with the aid of DTA, as was done with the products of step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in a water vapour atmosphere, the dependence of the amount of adsorbed water on temperature was determined. For this purpose the products of step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ were heated isothermally for 6 hours in the temperature range 100–400° in 13.3 kPa of D_2O vapour. The amount of water absorbed was then estimated on the basis of the size of the DTA peaks on subsequent heating of these samples. Figure 2 shows the temperature-dependences of the

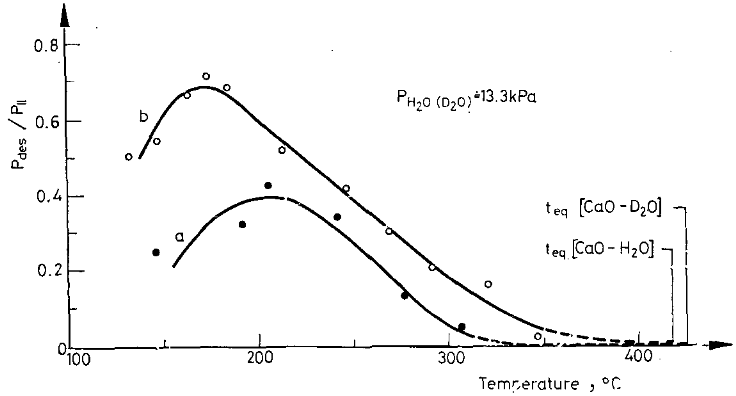

Fig. 2. Temperature-dependences of the ratios between the areas P_{des}/P_{II} of DTA peaks which correspond to the desorption and to step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ (curve *a*) and of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ (curve *b*) at a H_2O (D_2O) vapour pressure of 13.3 kPa.

Table 1

Decreases of D_2O (in moles) from one mole $3CaO \cdot Al_2O_3 \cdot 6D_2O$ according to TG curves in a laboratory atmosphere

Step I 200–410°	Step II 410–600°	Step III 600–880°	Total 200–880°
4.55	0.47	0.37	5.39

Table 2

Decreases of D_2O (in moles) from one mole $3CaO \cdot Al_2O_3 \cdot 6D_2O$ according to TG curves in a stationary nitrogen atmosphere

Step I	Step II		Total
210–410°	stage I 410–560°	stage II 560–900°	220–900°
4.53	0.72	0.24	5.49

ratios between the areas $P_{\mathrm{des}}/P_{\mathrm{II}}$ of the DTA peaks which correspond to desorption and to step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ and $3CaO \cdot Al_2O_3 \cdot 6H_2O$ [8]. From these curves it may be seen that the amount of water absorbed decreases with increasing temperature of isothermal heating. The sorption of D_2O by the products of step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ is considerably slower than the sorption of H_2O by the products of step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6H_2O$. The sizes of the crystals of the two starting materials were roughly identical (about 10 μm). This difference in the sorption capacity can be caused by a slower diffusion of the D_2O molecules into the grain boundaries of the products of step I of decomposition.

Release of the absorbed water is evidently the cause for the doubling of the DTA peaks which occurs in certain instances in the course of step I of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in the presence of water vapour. The sorption of water vapour by the decomposition products of step I of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ influences the mechanism of this process, as follows from [10].

The enthalpy changes occurring during step I of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$, as recorded by DSC-cell and by solution calorimetry, are given in Table 3.

Table 3

Enthalpy changes occurring during the first step of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ recorded with DSC cell and with solution calorimetry

$\Delta H_{r,\,I}$			
DSC		Solution calorimetry	
kJ/g	kJ/mole D_2O	kJ/g	kJ/mole D_2O
0.687	59.2	0.702	60.1

The second step of thermal decomposition

A comparison of the TG curves of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ recorded in a laboratory atmosphere with those recorded in a stationary nitrogen atmosphere (Fig. 1), as well as the phase analysis of the products of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in a CO_2 atmosphere, showed that step II of thermal decomposition in a laboratory atmosphere is distorted by the reaction of CO_2 with the decomposition products and by the subsequent decomposition of $CaCO_3$.

In this way at least one of the subsequent decomposition steps reported by some authors can be explained.

The first part of step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ took place so quickly, similarly to that of $3CaO \cdot Al_2O_3 \cdot 6H_2O$, that it was possible to record the corresponding enthalpy change in the calorimeter cell. For this reason we designated this part as stage 1 of step II (see also [8]). From Fig. 1 and Table 2 it follows that after this stage was finished water was released in further stages of the decomposition. These processes, however, are so slow that the sensitivity of our equipment did not allow recording of the enthalpy changes.

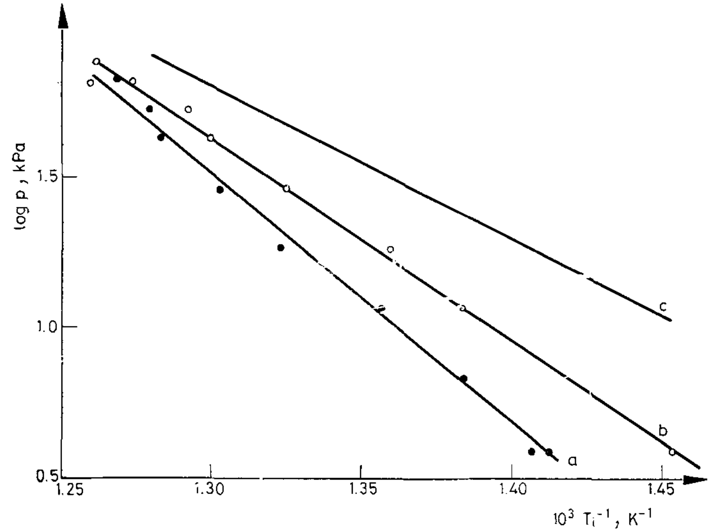

Fig. 3. Straight line *a* representing the dependence of the pressure *p* of D_2O vapour on the temperature of the beginning of DTA peak T_i, which corresponds to stage 1 of step II of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ decomposition. Line *b* represents the same dependence for a phase formed in the course of a 4-hour heating of the products of stage 1 of step II of decomposition in D_2O vapour at temperatures between the end of step I and the beginning of step II. Line *c* represents the equilibrium dependence of the vapour pressure of D_2O on temperature in the system $CaO-D_2O$.

By X-ray analysis the presence of CaO and of a phase whose diffraction diagram was almost identical with that of $12CaO \cdot 7Al_2O_3 \cdot (0-1)H_2O$ could be determined in the products of stage 1 of step II of decomposition. Since the temperature of the beginning of step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ depends on the pressure of the D_2O vapour, we assumed that step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ begins with dissociation of $Ca(OD)_2$. We tried to check the validity of this assumption, as we did when investigating the mechanism of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ [8], by finding the dependence of the temperature of the beginning of the second peak in DTA curves of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ on the pressure of the D_2O vapour, and by recording the enthalpy change in the course of stage 1 of step II of decomposition.

In Fig. 3 graphs of log *p* against $1/T_i$ are shown. The straight line *a*, corresponding to stage 1 of step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$, differs in its position and slope from line *c* which, according to [11], represents equilibrium in the system $CaO-D_2O$. The respective lines for $3CaO \cdot Al_2O_3 \cdot 6H_2O$ have a similar course. Line *c* differs from line *b*, which represents the pressure-dependence of the temperature of the beginning of thermal dissociation of $Ca(OD)_2$; the latter substance was formed in the reaction of D_2O vapour with reaction products of stage 1 of step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ in the course of a 4-hour period at temperatures between the end of step I and the beginning of step II of decomposition. Hence, we may assume, similarly as in our previous work [8], that the discrepancies between the courses of *a* and *c* may be due to the imprecision of the method used, or possibly to the lower activity of $Ca(OD)_2$ in the decomposition products of $3CaO \cdot Al_2O_3 \cdot 6D_2O$.

The enthalpy change in the course of stage 1 of step II of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ ($\Delta H_{r,II,1} = 0.127$ kJ/g, or 69.0 kJ/mole D_2O) corresponds to about 68% of the dissociation heat of $Ca(OD)_2$ (101.7 kJ/mole D_2O, 400–500° [11]). As in the case of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ [8], in this stage simultaneously with the thermal dissociation of $Ca(OD)_2$ further reactions take place which have enthalpy changes smaller than the dissociation heat of $Ca(OD)_2$.

Conclusion

As follows from the above measurements and from our previous work [8], the mechanisms of thermal decomposition of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $3CaO \cdot Al_2O_3 \cdot 6D_2O$ are similar. In step I (210–410°) $Ca(OH)_2$ and $Ca(OD)_2$, respectively, and certain disordered transition phases with structures similar to that of $12CaO \cdot 7Al_2O_3 \cdot (0-1)H_2O$ are formed. Absorption of water by products of step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6D_2O$ is considerably slower than in the case of $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

The values of $\Delta H_{r,I}$ for step I of decomposition of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and of $3CaO \cdot Al_2O_3 \cdot 6D_2O$, which are near to the dissociation enthalpies of many hydrates of inorganic substances (approximately 55 kJ/mole H_2O [11]) suggest that in the structures of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $3CaO \cdot Al_2O_3 \cdot 6D_2O$ most probably hydrogen-bonds are formed between OH^{-1} and OD^{-1} groups, respectively.

Step II of thermal decomposition of $3CaO \cdot Al_2O_3 . 6H_2O$ and $3CaO \cdot Al_2O_3 \cdot 6D_2O$ begins with the dissociation of $Ca(OH)_2$ and $Ca(OD)_2$, respectively. The enthalpy changes are smaller, however, than those of the thermal decomposition of $Ca(OH)_2$ and $Ca(OD)_2$, respectively. Hence, it follows that in the course of this stage of step II other simultaneous processes take place, with enthalpy changes smaller than the dissociation heats of $Ca(OH)_2$ and $Ca(OD)_2$.

At least one of the TG deflections which have been reported by various authors can be accounted for by the reaction of CaO – formed in step II of the thermal decomposition – with CO_2 from the ambient atmosphere and by the subsequent decomposition of $CaCO_3$.

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Résumé — On a étudié le mécanisme des deux premières étapes de la décomposition thermique de $3CaO \cdot Al_2O_3 \cdot 6D_2O$. La présence de $Ca(OD)_2$ a été mise en évidence dans les produits de la première étape de décomposition. Les variations d'enthalpie correspondant à la première et à la deuxième étape de la décomposition ont été mesurées à l'aide de la cellule calorimétrique du thermoanalyseur Dupont 990; elles s'élèvent respectivement à $\Delta H_{r,I} = 59.2$ kJ/mole D_2O pour l'étape I (210–410°) et $\Delta H_{r,II,1} = 69.0$ kJ/mole D_2O pour la première partie, rapide, de l'étape II («stade 1 de l'étape II», couvrant l'intervalle 410–560°). Ceci indique que la dissociation de $Ca(OD)_2$ n'est pas la seule transition qui ait lieu dans la première partie (stade 1) de l'étape II.

Zusammenfassung — Der Mechanismus der I und II Stufe der thermischen Zersetzung von $3CaO \cdot Al_2O_3 \cdot 6D_2O$ wurde untersucht. Die Gegenwart von $Ca(OD)_2$ wurde in den Produkten der ersten Zersetzungsstufe nachgewiesen. In der Kalorimeterzelle des Thermoanalysers Dupont 990 wurde die Enthalpieänderungen $\Delta H_{r,I}$ 59.2 kJ/Mol D_2O für Stufe I (210 bis 410°) und $\Delta H_{r,II,1} = 69.0$ kJ/Mol D_2O für den ersten schnellen Teil der Stufe II (»Etappe 1 der Stufe II«) im Temperaturbereich von 410 bis 560° gemessen. Dies zeigt, daß die Dissoziation von $Ca(OD)_2$ nicht der einzige Übergang in der ersten, schnellen Phase (Etappe 1) der Stufe II ist.

Резюме — Изучен механизм I и II стадий термического разложения $3CaO \cdot Al_2O_3 \cdot 6D_2O$. В продуктах I стадии разложения доказано наличие $Ca(OD)_2$. В калориметрической ячейке Дюпон 990 термоанализатора измеренное изменение энтальпии для первой стадии (210—410°) было $\Delta H_{r,I} = 59.2$ кдж/моль D_2O, а для первой быстрой части стадии II (часть 1 стадии II в температурном интервале 410—560°) изменение энтальпии составляло $\Delta H_{r,II,I} = 69.0$ кдж/моль D_2O. Это указывает на то, что диссоциация $Ca(OD)_2$ является не единственныч переходом, имеющим место в первой быстрой части (часть I) стадии II.