THERMAL ANALYSIS OF THE DISSOCIATION OF CARBONATE MATERIALS AT HIGH HEATING RATE

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The dissociation of carbonate materials under a high heating rate has been studied by means of specially constructed original apparatus which allows avoidance of the influence of gas diffusion on the decarbonation process, and acceleration of the measurements.

Decarbonation is a widely studied process and many authors [1, 2] cite this reaction as a classical example of heterogeneous topochemical transformations of an autocatalytic nature, proceeding according to the uniformly contracting spehere model. At the same time, the velocity of motion of the reaction boundary is frequently determined by the diffusion parameters of the reaction system which conceal the most rapid (chemical) stage of the process. Through the adequate preparation of a sample and the choice of a reactor in which the diffusion is of relatively low influence, it is possible to create conditions under which the reaction is limited by a chemical stage only [3]. A high velocity of the chemical stage requires an adequate rate of heat supply to the reaction zone. Such a velocity can be achieved by rapid heating of the sample, for instance by placing it is a reactor previously heated up to the dissociation temperature. However, it is difficult to attain the heating characteristics of the process, because the heat capacities of the heating arrangements in the existing installations for thermal analysis restrict the sample heating velocity; in practice, this does not exceed 20–40 deg/min [4, 5]. Information about thermal transformations of materials at high heating rates allows certain conclusions concerning not only these transformation effects and the energetic states of the resulting dissociation products, but also the kinetic aspects of the process.

We have proposed a simple and original apparatus for thermal analyses of the dissociation of carbonate materials, for instance calcium carbonate, heated up to the dissociation temperature within a few seconds.

The reactor comprises a U-shaped pipe, the bend of which, with its two thermocouples (inside and outside), is palced in the heating arrangement. Such a disposition of the thermocouples allows temperature measurement

both in the heating arrangement and inside the reactor. A carrier gas supply is connected to one of the open ends of the reactor. Through the other end, the sample under study can be introduced and the volatile reaction products can be removed. Compressed air removes solid dissociation products after analysis. Figure 1 shows the curve of the difference between the temperature of the reaction zone and the constant temperature of the heating arrangement after a calcite sample is introduced into the reactor. The area outlined by peak I characterizes the cooling and subsequent heating of the reaction zone, connected with the introduction of a sample at normal temperature into the heated reactor. Peak II is due to the change in heat content of the sample resulting from its dissociation. Point D on the curve corresponds to the initial moment of carrier gas being blown through the reaction zone, when the sample reaches the temperature of dissociation.
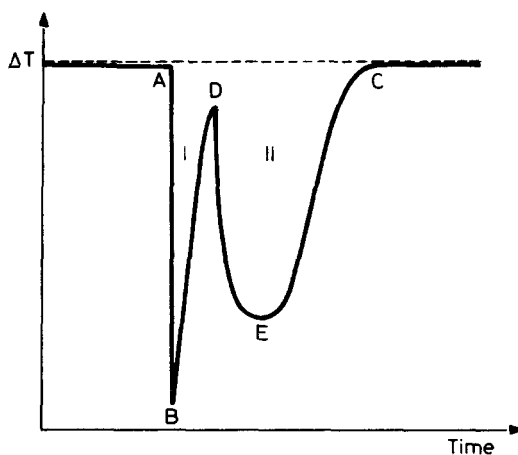

Fig. 1   Change of the reaction zone temperature during thermal dissociation of calcite.

The area of peak I determines the heat consumption for heating the sample from the normal temperature to the dissociation temperature. Its width indicates the heating duration, and the peak intensity depends on the thermal conductivity and heat content of the sample under study. According to theoretical considerations of differential thermal analysis (DTA−) [4, 5], the area of peak II is proportional to the change in the heat content of the sample during the dissociation. The width of peak II is determined by the time for complete decomposition of the carbonate sample.

The thermal effect of the thermal decomposition of calcium carbonate may be calculated via the following empirical equation:

$$Q = (2 - S'_T/S'_9)\, S''_T/S''_9 \cdot 1.76 \cdot 10^8 \text{ kJ/kg}$$

where S'_T, S'_9 and S''_T, S''_9 are the areas of peaks I and II in the diagrams of the studied sample and a standard. A sample of pure calcite was used as a standard.

The equation is based on the relation S''_T/S''_9, characterizing the deviation of the area of the endothermal effect of the dissociation of the carbonate sample as related to that of the standard. This relation is multiplied by the standard heat of dissociation of calcite, $-1.76\ 10^3$ kJ/kg.

The term in parentheses is chosen in accordance with the fact that the error in determining the thermal effect of the dissociation of the standard does not exceed $\pm 5.0\%$. S'_T/S'_9 characterizes the deviation of the physical parameters of the studied sample such as heat capacity and thermal conductivity, as related to those of the standard. The error in determining the time for the complete decomposition of calcite does not exceed $\pm 3.5\%$.

Obvious advantages of the proposed method are the absence of the zero line drift and the high speed of measurements. The latter is due to the short time required for each analysis (2–3 minutes), and to the fact that there is no need to cool the heating arrangement before each measurement. The method permits up to 100 analyses during a working day.

References

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Zusammenfassung — Die Dissoziation von Calciumcarbonat bei hoher Aufheizgeschwindigkeit wurde mit einer eigens entwickelten DTA-Apparatur untersucht, bei der der Einfluss der Gasdiffusion vermieden und die Messung beschleunigt werden kann.

РЕЗЮМЕ — С помощью специально сконструированного прибора изучена диссоциация карбонатных материалов при высоких скоростях нагрева, что позволяет избежать влияния диффузии на процесс декарбонизации и ускорить проведение исследований.