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APPLICATION OF DTA AND TG TO STUDIES OF THE $CaCO_3$–CaF_2 PHASE DIAGRAM

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A new method (based on DTA and TG) for the determination of the eutectic composition is proposed for systems in which one of the components is unstable in the vicinity of the eutectic melting temperature. The eutectic composition established by means of this method for the $CaCO_3$–CaF_2 system is in very good agreement with the results obtained in a classical way.

The experimental determination of phase diagrams in which eutectic melting occurs requires a whole series of measurements, carried out on mixtures with varying contents of one component. Each sample must first be heated till melting, and then several effects are registered during its cooling, the main ones being as follows: crystallization, phase transitions, and the formation and decomposition of chemical compounds or solid solutions. In the temperature versus cooling time curves, the presence of a eutectic is manifested by the appearance of straight lines parallel to the time axis, whose length is proportional to the amount of the phase being precipitated. In a binary system with a eutectic, the longest parallel distance corresponds to the eutectic point. From these data, with the use of Tamman's triangle, one can determine the composition of the eutectic point. In the case of the $CaCO_3$–CaF_2 system, in which the calcium carbonate decomposition temperature is close to the temperature of eutectic melting (880°, [1]), application of the above-described method is difficult since pressures of ca. 100 MPa are required in order to avoid the decomposition of $CaCO_3$.

The crystallization processes occurring either during cooling of the system or during its heating are correlated with clear thermal effects in the DTA curve. The area of the DTA peak is proportional, among others, to the mass of substance being investigated. It is therefore possible that in studies of phase diagrams the T vs. t curves be replaced by ΔT vs. t ones (T = temperature, t = time). The diagram can then be constructed by studying the relationship between the area of the DTA peak and the composition of the system.

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Experimental

The calcium carbonate used in the experiments was purchased from Riedel–De Haen (West Germany). Calcium fluoride (Hitachi, Japan) was heated at 1000° for 5 h before using mixed with calcium carbonate. Magnesium fluoride was prepared in the laboratory from magnesium oxide and hydrofluoric acid.

Simultaneous TG and DTA experiments were carried out on a Q–1500 D derivatograph (MOM, Hungary), within the temperature range 20–1000°, at a heating rate of 10 deg min^{-1}. High-purity alumina was used as the standard reference material.

Results and discussion

The physical properties, such as thermal conductivity or specific heat, of a two-component mixture may vary depending on its chemical composition. Therefore, in addition to Tammann's assumption, which states that the maximum effect corresponds to the composition of the eutectic, one must assume that the changes in composition do not affect the value of coefficient k, which correlates the amount of heat evolved with the area of the peak corresponding to a given transition.

In order to verify this assumption, we have determined the composition of the eutectic formed in the CaF_2–MgF_2 system. For ten mixtures in the composition range from 5 wt% to 90 wt% MgF_2, the DTA curves were recorded in the heating and in the cooling regime. A representative curve is presented in Fig. 1. From the relationship between the area of the endothermic peak and the percentage of MgF_2 in the sample, the eutectic composition can be determined (Fig. 2). The obtained value (55 wt% CaF_2, 45 wt% MgF_2) is in very good agreement with the data presented in the literature (55.6 wt% CaF_2, 44.4 wt% MgF_2) [2]. The eutectic composition was determined on the basis of experiments in which the eutectic melting temperature was only slightly exceeded.

The applied method enabled us to determine the eutectic composition for the $CaCO_3$–CaF_2 system, i.e. a system in which one of the components is unstable at temperatures close to the eutectic melting temperature. A series of samples with compositions in the range from 10 wt% to 90 wt% CaF_2 were studied by means of thermal analysis. The measurements were carried out in a CO_2 atmosphere in order to shift the decomposition temperature of calcium carbonate towards higher temperatures. In the DTA curves (Fig. 3), the endothermic effects of eutectic melting are obscured by the endothermic dissociation of $CaCO_3$. Therefore, the peak area is dependent not only on the amount of the eutectic mixture, but also on the quantity of calcium carbonate which decomposed up to the end of eutectic

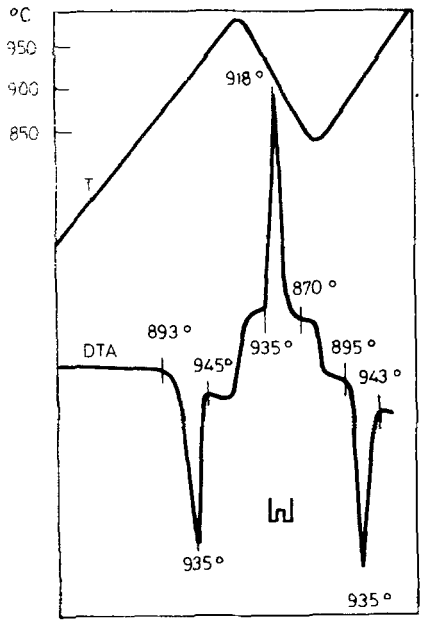

Fig. 1 T and DTA curves recorded during heating and cooling of the 90 wt% MgF_2 and 10 wt% CaF_2 mixture. $m = 1000$ mg, in air atmosphere

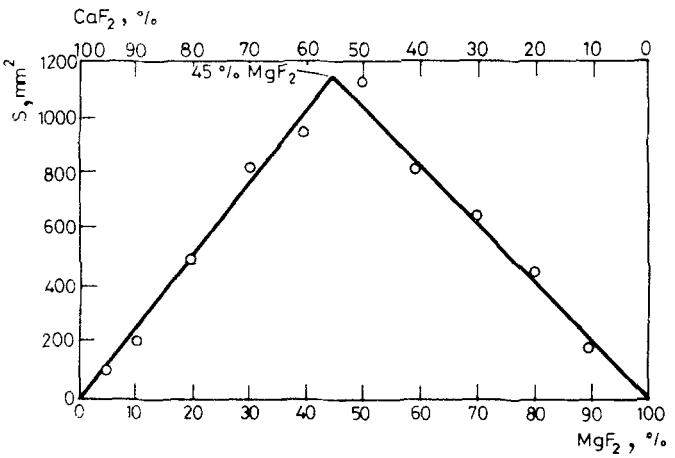

Fig. 2 The relationship between the composition of CaF_2–MgF_2 system and the area of the endothermic peak observed in DTA

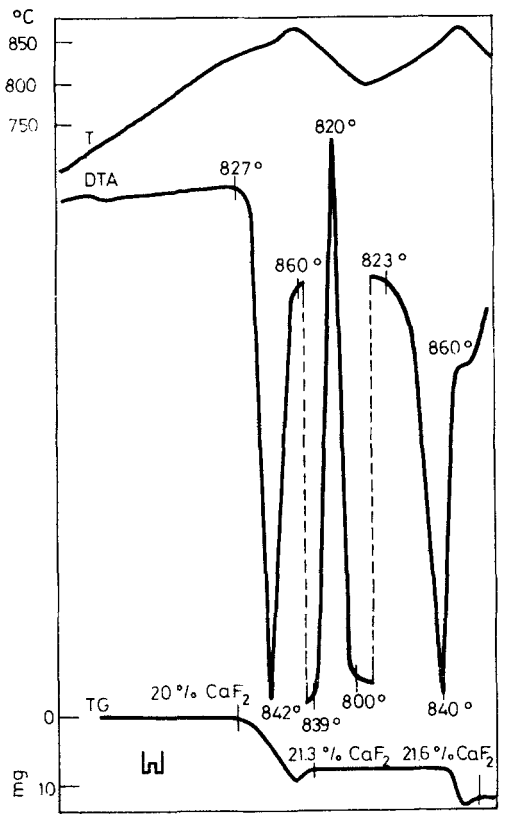

Fig. 3 T, TG and DTA curves recorded during heating and cooling of the 80 wt% $CaCO_3$ and 20 wt% CaF_2 mixture (CO_2 atmosphere) $m = 1000$ mg

melting. In order to separate these two effects, the DTA measurements in the cooling regime were recorded. The exothermic peak registered in this case was associated only with crystallization of the solid phase. The curves obtained in this manner were used to determine the relationship between the area of the exothermic peak and the percentage of CaF_2 in the system. A small correction due to the thermal dissociation of $CaCO_3$ was taken into account (TG curve in Fig. 3). The determined eutectic composition was 36.5 wt% CaF_2 and 63.5 wt% $CaCO_3$ (Fig. 4), which is in close agreement with the result obtained by Gittins and Tuttle [1], who reported a eutectic composition of 36 wt% CaF_2 and 64 wt% $CaCO_3$ on the basis of measurements carried out under a pressure of 100 MPa in order to avoid the decomposition of $CaCO_3$.

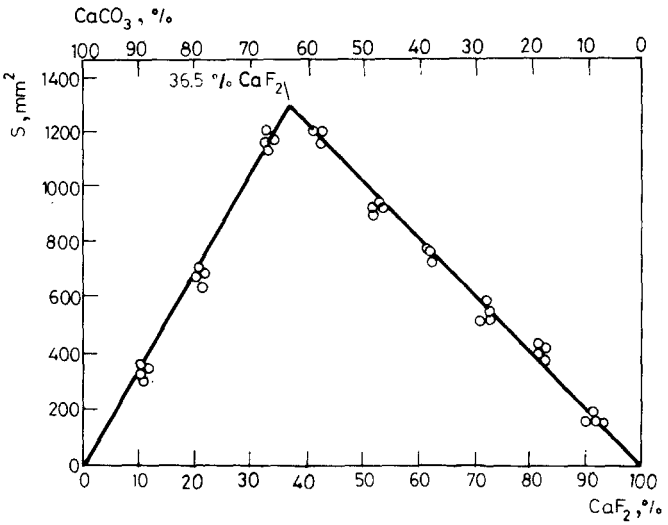

Fig. 4 The relationship between the composition of $CaCO_3$–CaF_2 system and the area of the exothermic peak in DTA

References

1 J. Gittins and O. F. Tuttle, Am. J. Sci., 262 (1964) 66.

2 M. Rolin and M. Clausier, Rev. Int. Hautes Temper. et Refract., 4 (1967) 39.

Zusammenfassung — Eine neue Methode zur Bestimmung der eutektischen Zusammensetzung von Systemen, deren eine Komponente in der Nähe der eutektischen Temperatur instabil ist, beruht auf der simultanen TG-Messung. Mit der vorgeschlagenen Methode wird die eutektische Zusammensetzung des Systems CaF_2–$CaCO_3$ in sehr guter Übereinstimmung mit den Ergebnissen klassischer Untersuchungen gefunden.

Резюме — На основе ДТА и ТГ предложен новый метод определения состава эвтектики для систем, в которых одна из компонент неустойчива вблизи температуры плавления эвтектики. Состав эвтектики, установленный предложенным методом для системы $CaCO_3$–CaF_2, хорошо согласуется с результатами, полученными классическим методом.