Journal of Thermal Analysis, Vol. 16 (1979) 399—406

QUASI-ISOTHERMAL THERMODILATOMETRY

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(Received March 10, 1978)

A measuring technique has been developed whereby thermodilatometric examinations can be carried out at a strictly constant rate, slower by one or two orders of magnitude than that of conventional measurements. Under the special conditions the temperature of the sample changes in a special way. The TD curve recorded as a function of this temperature yields new information about the kinetics and mechanism of the structural changes taking place within the sample.

On the basis of favourable experience gained with our earlier quasi-isothermal and quasi-isobaric thermogravimetric [1, 2] and the simultaneous thermogravimetric and thermogastitrimetric [3] techniques, we developed a new method [4] with the help of which thermodilatometric (TD) examinations too can be carried out under quasi-isothermal conditions. We set out from the idea that not only the courses of those decomposition reactions which can be examined by TG may be influenced advantageously by the quasi-isothermal heating technique; favourable effect could also be exerted upon the performance of all those processes which can be followed by TD, e.g. solid-phase reactions, changes in crystal modification, or recrystallization, if in a similar way the rate of transformation is decreased by one or two orders of magnitude.

The principle of the device suitable for the performance of such examinations is shown in Fig. 1. The sample, compressed into a tablet (1), is situated between a stationary quartz rod (3), fixed to the column of the balance, and another mobile quartz tube (2), fixed to the balance arm. Accordingly, the magnitude of the electric signal induced in the differential transformer (9) upon the moving of the balance arm is proportional to the change occurring in the length of the tablet, while the signal of the deriving system consisting of a magnet (8) and coil (7) is proportional to the rate of the changes taking place in the length of the test piece. Thus, if the conventional dynamic heating programme (D) is applied, the recording device (10) records the conventional dilatation curve (TD) and its derivative (DTD).

If we wish to apply the new quasi-isothermal heating technique (Q) instead of the dynamic heating programme, then we couple the deriving unit (7, 8) by means of a switcher (14) with a sensor-controller (12), instead of the recording device (10), as shown in Fig. 1. With the mediation of the heating programmer (13), the sensor-controller reduces the voltage of the heating current every time the voltage of the derived signal, i.e. the rate of the process, reaches a minute threshold value, and immediately increases the voltage again if the rate of the process drops below this value. In this way a difference can be established between the furnace and sample temperatures such that the changes in the size of the sample, i.e. the process examined, should take place at a minute and constant rate. As a consequence, the temperature of the sample changes in a special way. As Fig. 2 shows, in the case of the TD curve recorded as a function of this temperature curve, the rate of the process is the independent variable (see curve 2), while the temperature (curve 1) is the dependent one, i.e. the situation is just the reverse of that for conventional TD curves.

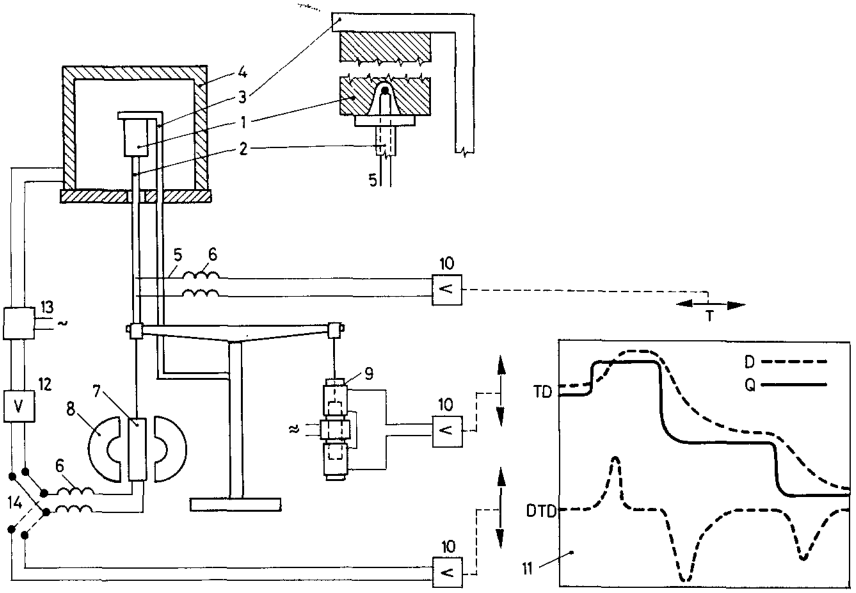

Fig. 1. Derivatograph for quasi-isothermal TD and TG resp. and dynamic TD, DTD and TG, DTG resp. 1. Testpiece, 2. silica tube, 3. silica rod, 4. furnace, 5. thermo-couple, 6. flexible conductor, 7. coil, 8. magnet, 9. differential transformer, 10. recorder, 11. chart, 12. sensor-controller, 13. heating programmer, 14. switcher

The dynamic and quasi-isothermal TG curves can be traced in similar way in a second experiment by applying a new sample. The only difference is that the compressed sample (1) does not lean against the fixed stationary quartz rod (3), and as a consequence the balance, not hindered in its moving, measures the weight change of the test piece and not the changes occurring in its length.

The TD curves of Fig. 2 demonstrate the process of spinel formation in the solid phase between ZnO and Fe_2O_3 as functions of time (curve 2) and temperature (curve 3). According to curve 4, the length of the tablet, compressed from powdered

ZnO and Fe_2O_3 mixed in stoichiometric proportions, increased by about 2.7% between 570 and 700° while between 700 and 1000° it decreased by about 5%. These processes can be interpreted more easily on the basis of Fig. 3.

As long as forty years ago, Hüttig [5] thoroughly studied the solid-phase reaction between ZnO and Fe_2O_3 and stated that the transformation begins already at about 300° though only in the surface layers of the grains. The results of his various examinations, which are also indicated in Fig. 3, serve as a proof of this finding. Hüttig examined the changes at increasing temperature in the catalytic effect of the mixture of ZnO and Fe_2O_3 upon the reaction $CO + 0.5\ O_2 = CO_2$ (curve 1). Curve 2 represents the variations in the adsorption capacity of water vapour, curve 3 those in the magnetic susceptibility, curve 4 those in the specific weight and curve 5 those in the intensity of the characteristic X-ray line of $ZnFe_2O_4$.

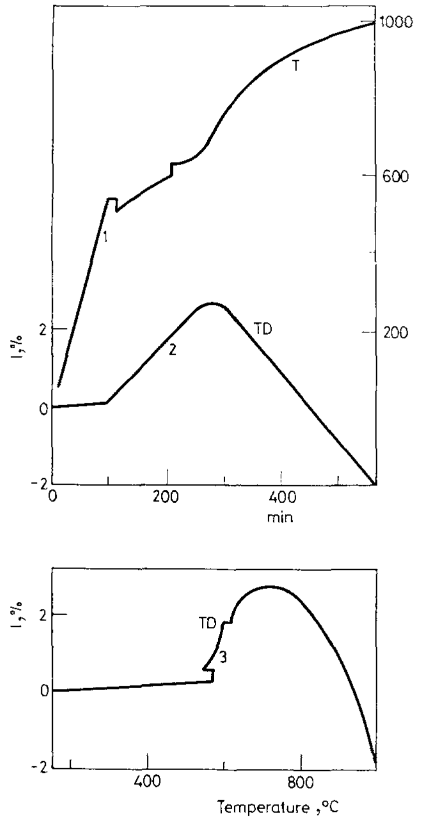

Fig. 2. TD, DTD and T curves of Fe_2O_3 + ZnO mixture traced under quasi-isothermal heating conditions. Curves 1, 2 and 3, traced against time, curve 4. against temperature

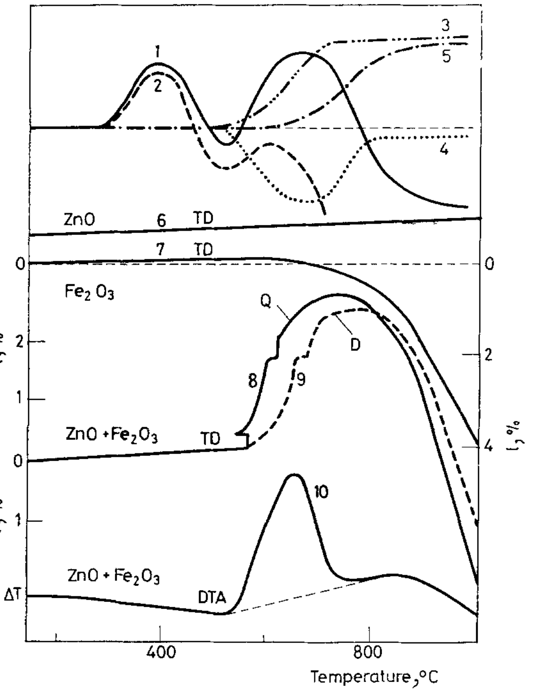

Fig. 3. Various changes during spinell-formation. 1. Catalytical effect of the mixture exerted upon the reaction $CO + O.5\ O_2 = CO_2$, 2. variations of the adsorption capacity of water vapour, 3. variations in magnetic susceptibility, 4. changes in specific weight, 5. changes in intensity of the X-ray lines of $ZnFe_2O_4$, 6, 7 and 8, TD curves obtained under quasi isothermal (Q) and 9. under dynamic (D) heating conditions, 10. DTA curve

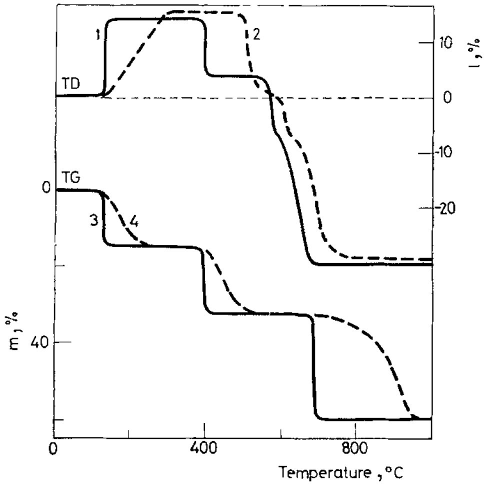

Fig. 4. TD and TG curves of $CaC_2O_4.H_2O$. Curves 1 and 3 traced under quasi-isothermal (Q) and curves 2 and 4 under dynamic (D) heating conditions

The second period of the transformation, in which directed volume diffusion already plays the main role, begins at 570°. This latter process can be followed by the quasi-isothermal TD method. Both, the curve obtained by using dynamic heating (curve 9) and that traced under quasi-isothermal heating conditions (curve 8) indicated a significant expansion of the test piece between 570 and 700°. It is noteworthy that this process began at nearly the same temperature as that at which the contraction of Fe_2O_3 started (curve 7) when, through self-diffusion, the recrystallization of Fe_2O_3 began, i.e. its lattice elements became mobile. Fe_2O_3 was prepared from $Fe_2O_3 \cdot H_2O$ by heating at a temperature not higher than 600° in order to avoid recrystallization.

The process of spinel formation ended at about 700°. Thereafter, as curves 8 and 9 illustrate, the test piece began to contract; this can be explained by the recrystallization of the sample, i.e. the "mending" of the defective sites in the new phase.

In the temperature interval 500–700° there is a certain difference between the courses of TD curves obtained under dynamic and quasi-isothermal heating conditions, indicating that the variation in the heating rate influences strongly the rate of spinel formation and only slightly the recrystallization process. Figure 4 depicts the TD and TG curves of $CaC_2O_4 \cdot H_2O$ obtained under the conditions of the two different kinds of heating technique.

As the TG curve (curve 4) shows, the material lost its crystal water content at about 200°; according to the TD curve (curve 2), this caused the expansion of the test piece in contrast with expectations.

When dynamic heating was applied, the changes in weight and volume due to dehydration occurred in a temperature interval extending over ca. 100°. In contrast with this, under quasi-isothermal heating conditions (curves 1 and 3) the transformation took place at the strictly constant temperature of 150°. For both, the TG and TD curves, the spontaneous stabilization of the temperature proves that under given conditions the partial pressure of water vapour stays constant in the vicinity of the solid phase even if the material is examined not as a powder sample [1, 2], but as a compressed test piece. However, it also proves that the progress of transformation is influenced solely by the heat transport, i.e. by a physical process independent of the changes taking place in the concentration of the material, and thus the reaction is of zero order.

It is also noteworthy that the courses of the corresponding TD and TG curves are strictly parallel. This indicates that if the changes in the volume of the sample were the result of several processes (changes in crystal structure, formation and growth of the nuclei of the new solid phase, recrystallization, etc.) the partial processes would not have separated even if the rate of transformation had been reduced by several orders of magnitude.

From this aspect the situation is just the reverse with the decomposition of CaC_2O_4. The TD curves show the decomposition of anhydrous CaC_2O_4 to be a several-stage process, while the TG curves represent it as a strictly one-stage reaction. According to curve 3, the decomposition of the material took place at 380°. This coincides with the first shrinkage-indicating period of curve 1. The second shrinkage-causing process takes place at significantly higher temperature: 570 – 700°. It can be stated with great probability that in this temperature interval calcium carbonate underwent recrystallization. The two processes can be distinguished clearly only in the TD curve obtained by using the new measuring technique.

The TD curves do not indicate the decomposition of $CaCO_3$ at all. This is in accordance with earlier topochemical observations, according to which CaO, "remembering" the compound from which it was prepared, exhibits different chemical and physical properties from case to case. A simple explanation of this phenomenon is that the new solid product preserves the shape and size of the grains of the starting compound. Since the recrystallization of CaO takes place above 1000°, it could not be observed in the given case.

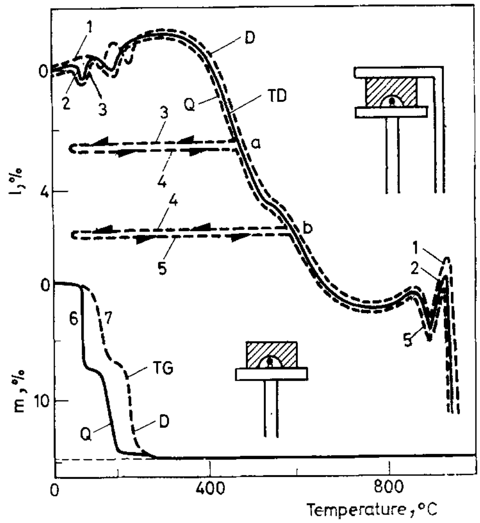

Fig. 5. TD and TG curves of $BaCl_2.2\ H_2O$. Curves 1 and 7 traced under dynamic, curves 2, 3, 4, 5 and 6 under quasi-isothermal heating conditions

Figure 5 demonstrates the TD and TG curves of $BaCl_2 \cdot 2\ H_2O$ obtained under the conditions of the two kinds of heating technique. According to the TG curves, the sample lost its crystal water content up to 300°. Thereupon, as shown earlier [6], between 300 and 800° a recrystallization process took place. Finally, before melting at 960° the material underwent a modification change at 920°. Of these processes, the recrystallization deserves special attention.

Curve 2 was obtained in 2000 minutes under the application of the quasi-isothermal heating technique. In this way the recrystallization took place about 50 times more slowly than in the case of curve 1, which was obtained by using a dynamic heating rate of 10°/min. Despite this circumstance, the courses of the two kinds of TD curve were nearly congruent. This proves that in the range investigated the course of the recrystallization was independent of the rate of the changes occurring in the sample temperature. However, this apparent contradiction becomes understandable if we consider that the rate of the directed diffusion, which makes rearrangement of the lattice elements possible, as well as the rates of nucleus formation and nucleus growth, which establish the formation of the new inner order, are in exponential relationship with temperature. Consequently, at every temperature the state which corresponds to the actual temperature is rapidly established.

Apart from the fact that the closest causal relationship exists between temperature and the progress of recrystallization, other proofs can also be found in curves 3, 4 and 5. These TD curves were traced on three successive days, the examination having been interrupted every evening and continued the next morning. The curves prove that the recrystallization process continued at the point where it had been stopped the previous day. This means that in every period of the recrystallization a certain temperature is necessary for the beginning of the process. This temperature value depends on the actual dispersity degree of the material and inner order of its grains. If the material has already attained a defined degree of rearrangement, then a higher temperature is necessary for the further increasing of this order.

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The authors thank Prof. E. Pungor for his interest in this work, and Mr. M. Arnold for his valuable help.

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Résumé — Les auteurs ont développé une technique de mesures qui permet d'effectuer les examens de thermodilatométrie à une vitesse strictement constante et inférieure, de un à deux ordres de grandeur, à celles des mesures conventionnelles. Suivant les conditions particulières, la température de l'échantillon varie d'une façon déterminée. Selon l'expérience, la courbe TD enregistrée en fonction de la température, donne des renseignements nouveaux sur la cinétique et le mécanisme des changements structuraux qui se produisent dans l'échantillon.

ZUSAMMENFASSUNG — Die Autoren entwickelten eine Meßtechnik für thermodilatometrische Untersuchungen bei streng konstanter Geschwindigkeit, welche um ein bis zwei Größenordnungen langsamer ist als die der üblichen Messungen. Den besonderen Bedingungen gemäß ändert sich die Temperatur der Proben in einer besonderen Weise. Laut Erfahrungen gibt die als Funktion dieser Temperatur aufgezeichnete TG-Kurve neue Informationen über Kinetik und Mechanismus der Strukturänderungen im Inneren der Probe.

Резюме — Авторы разработали технику измерений, с помощью которой могут быть выполнены термодилатометрические исследования при строго постоянной скорости, которая на один или два порядка ниже по сравнению с обычными измерениями. Согласно специфическим условиям температура образца изменяется особым путем. Согласно эксперименту, кривые ТД, регистрируемые как функция этой температуры, дают новую информацию о кинетике и механизме структурных изменений внутри образца.