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THE USE OF THE TEMPERATURE SIGNAL AND ITS DERIVATIVE IN A TG-DTA SIMULTANEOUS UNIT

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Abstract

Simultaneous TG-DTA units have a work station which allows plots to be made of temperature against time, as well as the conventional TG and DTA plots. These time–temperature plots and their derivatives can be used to show details of both exothermic and endothermic events. The melting behavior of zinc is used as illustrative of endothermic phase changes. Solid–solid transitions are exemplified by noting the transitions in quartz. Examples of chemical reactions being treated to temperature–time plots are the decomposition's of zinc oxalate in nitrogen (an endothermic event) and the oxidation of carbon black in air (a sustained exothermic event). This wide selection of exothermic and endothermic events serves to illustrate the details which can be drawn from any thermogravimetric plot irrespective of the other associated equipment present, which serves to reinforce the data presented in the present study.

Keywords: aluminum, carbon black, DTA, indium, TG, zinc, zinc oxalate

Introduction

In any thermogravimetry unit (TG) there are two plots available which are utilized in the present study, a plot of percentage mass loss plotted against temperature and a plot of temperature plotted against time. In most studies this latter plot is supposed to be the control imposed on the equipment and may simply be noted as a heating rate, for example as $10^{\circ}C\ min^{-1}$ or whatever rate is imposed on the system [1]. In fact as has been pointed out, the actual plot of temperature against time shows perturbations whenever an endothermic or exothermic event occurs [2]. These perturbations may be good enough to show on the plot of temperature (T) *vs.* time (t), but if the perturbations is small it will show on the plot of the first derivative of temperature (dT/dt) *vs.* time (t). In a recent publication these perturbations were used to produce DTA signals from a single pan, single thermocouple arrangement from signals generated from a TA instruments simultaneous TG-DTA unit, so that the single pan DTA signal could be compared against a conventional DTA signal. There was no need to modify the equipment,

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as the versatility of the unit and the work station enabled the appropriate plots to be generated very easily. The idea of using a single pan arrangement for differential thermal analysis is not new, and both Le Chatelier [3] and Roberts-Austin [4] used this method initially. The main purpose in adding a reference or control sample was to enable smaller temperature differences to be detected, especially as in those earlier days, detection was by means of galvanometric instruments where a span of 1000°C occurred in about 10 inches. The main drawback to these early attempts was the inherent insensitivity to very small and broad temperature changes. In the use of equipment available at present, the plot of temperature against time indicates the heating rate, while the first derivative plot indicates both the accuracy of that control and the perturbation occurring in the regions of endothermic and exothermic events. These advances in instrumentation enable the signal generated from a time–temperature plot in any TG experimental to be used to generate data on the endothermic or exothermic character of the change which is taking place. In the present study, this is illustrated by consideration of the melting of zinc. The illustration of the effectiveness of the method is shown also by reference to solid–solid transitions in quartz and to various chemical reactions, some endothermic and others exothermic.

Materials and methods

The thermogravimetry experiments were conducted using a simultaneous TG-DTA unit from TA instruments. The metal samples were heated in an atmosphere of flowing dry argon at a heating rate of 10°C min^{-1}. Alumina crucibles were used with empty sample pans used as reference. Zinc wire, certified as 99.99% pure was supplied by Aldrich Chemicals. Zinc oxalate dihydrate was purchased from Pfaltz & Bauer, Inc. It was heated in an atmosphere of flowing dry nitrogen on the TG balance. Silica was from U S Silica, and was also heated in an atmosphere of dry nitrogen. The carbon black was purchased from Colombian Chemical Co.

Results and discussion

A DTA signal [5] indicates the region where an endothermic or exothermic event occurs, depending on the direction in which the signal deviates from the projected baseline (Schematic, Fig. 1). In similar fashion a plot of time against temperature also projects the same deviation, located at the region where the thermal transition transpires, as portrayed schematically in Fig. 2. If however, the event is minor, it may go unnoticed from a plot of time against temperature, however the derivative of time against temperature conveys the same information (Fig. 3).

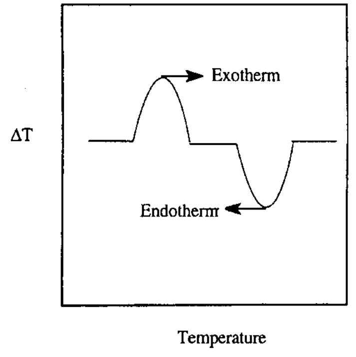

Fig. 1 Schematic diagram showing the occurrence of an endothermic and an exothermic event on the DTA plot

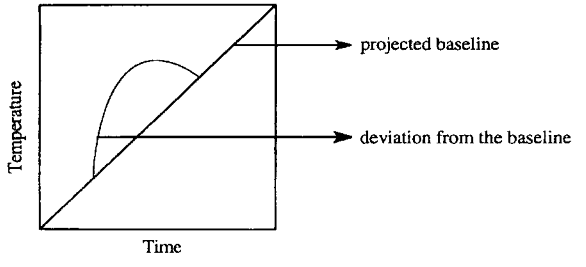

Fig. 2 Schematic diagram showing the occurrence of an exothermic event on the time–temperature plot

In this study indium, aluminum and gold were used to establish a three-point temperature calibration on the TG-DTA unit. The temperatures for the melting point of these metals were those taken from the literature [6], indium 156.4°C, aluminum, *m.p.* 660.4°C and gold 960.1°C. The conventional DTA signal from the TG-DTA unit for zinc is shown in Fig. 4. This is a thermal event not accompanied by a mass change. The plot of temperature–time shows the exact region where the temperature deviated from the baseline (Fig. 5).

In another study zinc oxalate dihydrate [7] was heated on the TG unit, under an atmosphere of flowing dry nitrogen (Fig. 6). As can be seen from the plot, it undergoes a two step degradation pattern. In the first stage, there is a mass loss which occurs at 150°C, where 18% of the mass is lost due to dehydration. The second stage occurs at 410°C which corresponds to decomposition. A plot of temperature against time shows no significant deviation in T *vs.* t but a deviation in dT/dt *vs.* t is readily apparent and corresponds to the first and second stage of the mass change (also Fig. 6). The plot reproduced here shows the derivative time–temperature data plotted superimposed on the TG data.

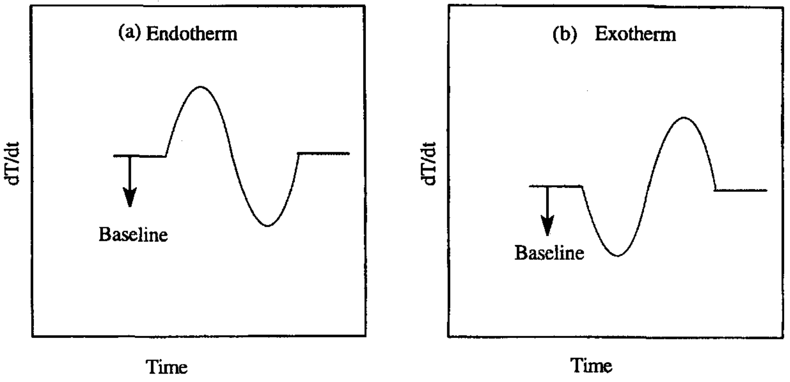

Fig. 3 Schematic diagram showing the occurrence of an (a) endothermic and (b) exothermic event on the derivative time–temperature plot

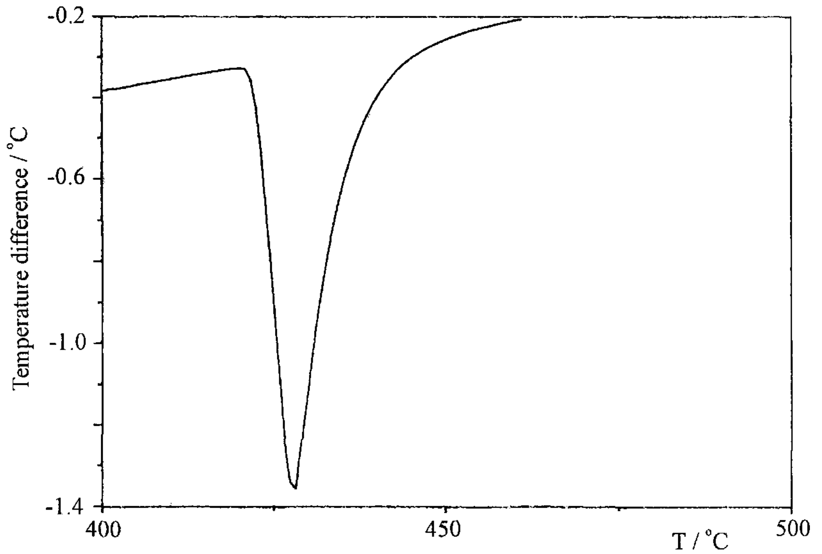

Fig. 4 DTA plot for the melting of zinc wire

A similar study on solid–solid transitions in quartz were also examined in an atmosphere of flowing nitrogen [8] where there is a reversible solid phase transition that occurs at 569.38°C (T_i) with a peak temperature (T_p) of 578.66°C. This change appears on the time–temperature plot as an endothermic event (Fig. 7). As can be seen from the figure, the derivative time–temperature also has a T_i at the same temperature and shows two peak temperatures, one at 576.23°C and the other at 580.74°C. The average of the two corresponds quite closely to the peak temperature shown by the DTA plot.

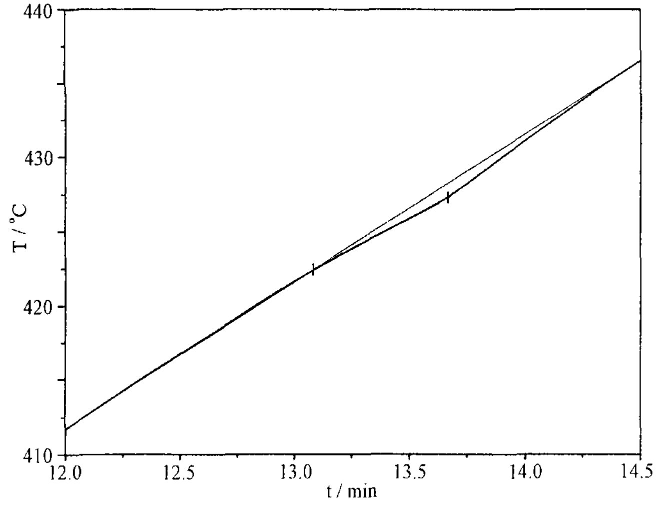

Fig. 5 Time–temperature plot showing the region where zinc melts

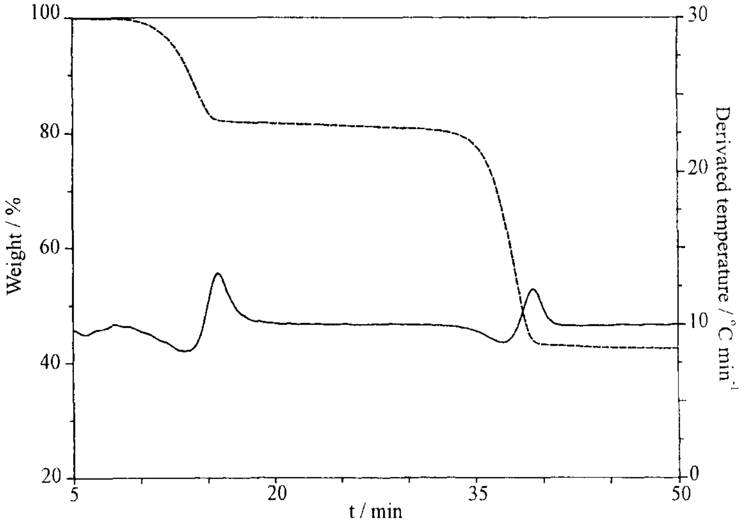

Fig. 6 TG and first derivative plot for time *vs*. temperature, for zinc oxalate dihydrate in an atmosphere of flowing nitrogen

To show how the time *vs*. temperature plot can also be used for exothermic events, the oxidation of carbon black was examined in an atmosphere of flowing dry air [9]. As can be seen from the TG plot, (Fig. 8) there is a loss in mass that occurs at 400°C that is exothermic and can be seen quite clearly on the time–temperature plot as a blip pointing in the upward direction. (Fig. 9). The characteristic shape of the first derivative plot allows the endothermic character of the

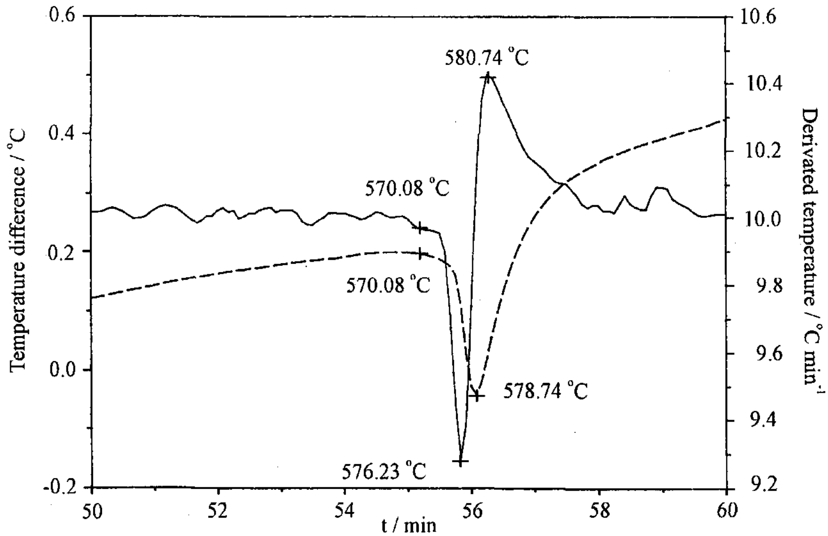

Fig. 7 DTA plot and derivative plot of time *vs.* temperature showing solid–solid phase transition for quartz

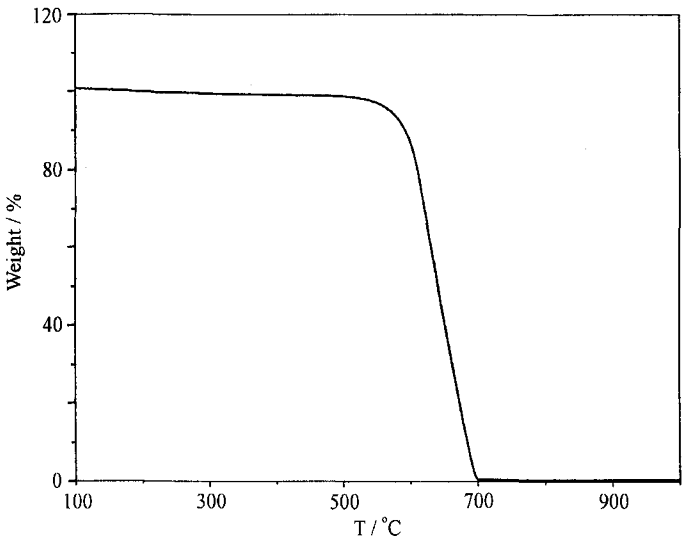

Fig. 8 TG plot for the oxidation of carbon black

event to be easily established. The exothermic event shows the first derivative plot initially deviating from the baseline in the upward direction, as portrayed in the schematic diagram earlier (Fig. 2), followed by several large exotherms, and a final endotherm, occurring when all the material burns off.

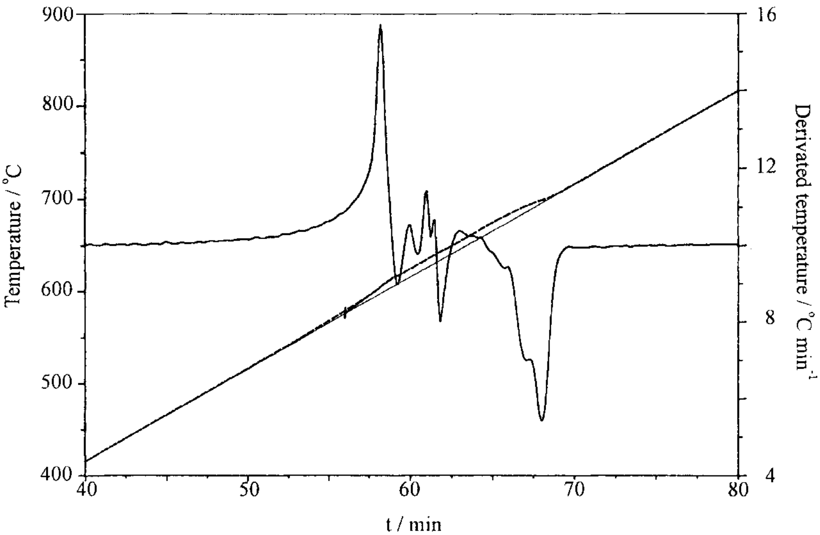

Fig. 9 Time–temperature plot and derivative time temperature plot of carbon black showing the occurrence of an exothermic event

Conclusions

The signals generated from a TG-DTA unit enable the % mass loss to be recorded against temperature but the extra presence of the DTA signal enables the endothermic or exothermic character of a thermal event such as zinc oxalate, carbon black and quartz to be determined for these processes where thermal reactions occur. The presence of a DTA signal also enables the thermal event to be characterized for phase-transitions not accompanied by mass change. However it is determined here that all these thermal events can be shown from the temperature–time plots or the first derivative of the temperature against time plots. If desired a signal very similar to the DTA plot can also be obtained, but the work station response showing a temperature–time plot and a derivative temperature–time plot provides easily accessible equivalent information. The fact that significant perturbations occur in the temperature–time plot in the region of thermal events has some significance in kinetic and thermodynamic considerations of changes which are taking place.

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