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DEVELOPMENT AND APPLICATIONS OF SAMPLE CONTROLLED THERMOMICROSCOPY

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Introduction

Sample controlled thermal analysis techniques such as constant rate transformation analysis or stepwise isothermal analysis, where the transformation rate of the sample itself is used to control the experiment, are becoming increasingly important [1]. The measurements are normally carried out using changes in the sample mass, sample dimensions or in the evolved gas, as the property used to control the experiment, and enable reactions to be studied in greater detail than is possible using linear heating techniques. A new approach is described here where a thermomicroscopy system has been developed to enable the intensity of the light reflected or transmitted by the sample to be used as the controlling signal [2].

Experimental

A block diagram of the system is shown in Fig. 1. The measurements have been carried out using a Linkam Model THMS600 hot stage. This unit operates over the range –180 to 600°C and uses a silver block heater in conjunction with a liquid nitrogen cooling system. Samples can be run in a controlled atmosphere and the fast response of the system makes it ideal for sample controlled studies. The intensity of the light signal from the sample

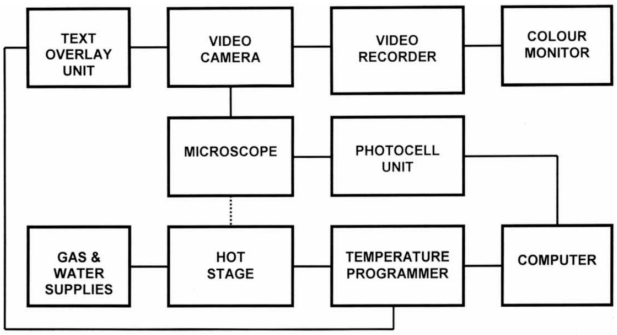

Fig. 1 Block diagram of sample controlled thermomicroscopy system

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was monitored by a silicon photodetector fitted into one eyepiece of a Nikon Labophot microscope. The standard temperature control system has been modified so that the sample temperature is controlled by the rate of change of the light intensity signal. The light intensity and sample temperature signals were recorded using a computer fitted with a Strawberry Tree 16-bit dynamic range data acquisition board.

Reflected light intensity measurements (RLI) were performed using white light [3]. In addition, depolarised light intensity (DLI) measurements have been carried out with transmitted polarised light. Crossed-polars were used so that the only light transmitted was due to the rotation of the polarised light by the crystalline structure of the sample [4, 5]. A number of control strategies have been implemented including constant transformation rate measurements and stepwise isothermal analysis.

Results and discussion

Decomposition of silver oxide under reflected light conditions

The decomposition of silver(I) oxide was chosen since it produces a well-defined colour change from black to white on decomposition to form the metal. An experiment carried out under constant rate (CR) conditions is shown in Fig. 2.

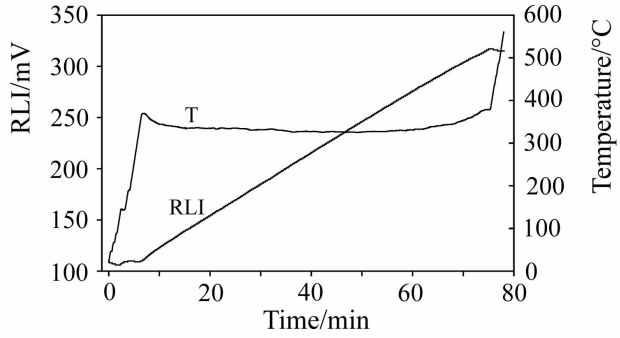

Fig. 2 Constant rate reflected light intensity curves for the decomposition of silver(I) oxide

The sample temperature can be seen to reduce rapidly once the reaction has started. This is typical of a nucleation reaction and was also observed in sample controlled studies where oxygen evolution was used to control the rate of decomposition. The sample temperature is then maintained essentially constant to enable a linear rate of reaction to be established over the complete decomposition reaction. Figure 3 shows a comparison of the sample controlled experiment with an experiment made under linear heating conditions at 10°C min^{-1} and illustrates the markedly lower temperature of reaction in the former case.

Transmitted light intensity measurements

The ability to study phase transformation under polarised light offers the potential to apply sample controlled techniques to a range of tranformations which do not take

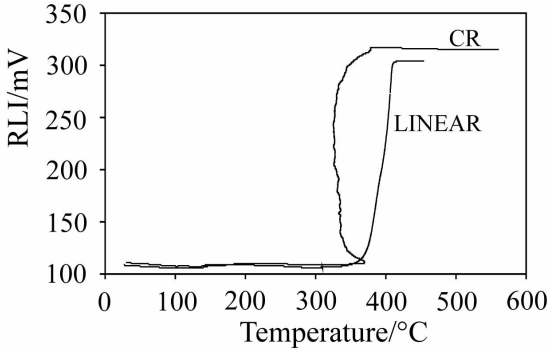

Fig. 3 Constant rate and linear heating reflected light intensity curves for the decomposition of silver(I) oxide

place with a change in mass. These include fusion, solid-solid transitions and recrystallisation reactions.

This is illustrated in Fig. 4 by a study of the behaviour of a crude oil on cooling under constant rate conditions. As the sample is cooled below room temperature the DLI signal begins to increase due to wax formation. In order to maintain a constant rate of wax formation the sample has to be cooled at a linear rate. This suggests that the amount of wax formed is directly related to the temperature and that there are no large hysteresis effects. Similar results were obtained using a DLI-stepwise isothermal approach.

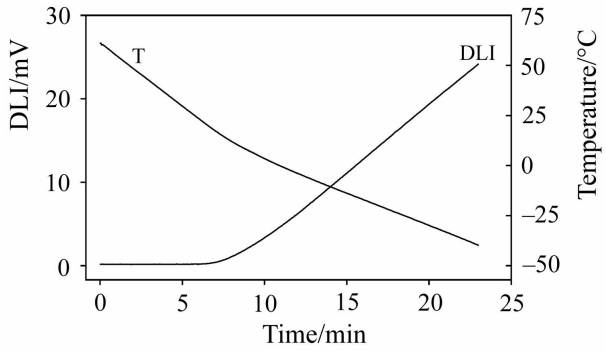

Fig. 4 Constant rate depolarised light intensity curves obtained under cooling conditions for a crude oil

In conclusion, a new range of sample controlled thermomicroscopy techniques have been developed which enables samples to be studied under reflected light or transmitted light conditions. The ability to make depolarised light intensity measurements should be of particular benefit in studying transitions in a wide range of materials including polymers, pharmaceuticals and liquid crystals.

References

1 P. A. Barnes, G. M. B. Parkes and E. L. Charsley, Anal. Chem., 66 (1994) 2226.
2 E. L. Charsley, C. Stewart, P. A. Barnes and G. M. B. Parkes, Paper presented at the 11th International Congress on Thermal Analysis and Calorimetry, Philadelphia, USA 1996.
3 J. H. McGill, Polymer, 2 (1961) 221.
4 E. L. Charsley and A. C. F. Kamp, Thermal Analysis, Vol.1, Ed. H. G. Wiedemann, Birkhauser Verlag 1972, p. 499.
5 E. L. Charsley, A. C. F. Kamp and J. A. Rumsey, Thermal Analysis, Vol.1, Ed. H. G. Wiedemann, Birkhauser Verlag 1980, p. 285.