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A THERMOMECHANICAL ANALYSIS STUDY OF SELECTED COMPOUNDS

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The TG and DTA profiles of compounds such as calcium oxalate monohydrate and copper sulfate pentahydrate are well known. A TMA study of these and other compounds is presented which, in addition to providing interesting data on the physical nature of phase changes and decomposition temperature ranges, confirms the classification of TMA as a principal thermal analysis technique.

Of the four principal thermal analysis techniques, Thermomechanical Analysis (TMA) is the least well known and applications are not as numerous as for the more well known techniques such as TG and DTA. TMA is a versatile technique which essentially determines dimensional changes as a function of temperature under applied conditions of compression, tension or zero load. TMA can also be used as a dilatometer to measure coefficients of expansion over wide temperature ranges. It can also be used to measure the behaviour of fibres under tension, the extent of penetration of materials under load as a function of temperature or time and for a study of various phenomena such as softening points, glass transition temperatures, solid-state and solid-liquid phase changes, shrink temperatures and the tracing of thermal histories.

Previous specific applications of TMA include the detection of solid state phase transitions associated with $KAsF_6$, $KC_2H_5SO_4$ and $Co(py)_2Cl_2$, a

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study of the deaquation of $BaCl_2.2H_2O$ and the fusion of acetanilide [1]. Simultaneous DTA/EGA/TMA studies of inorganic compounds such as $Ca(OH)_2$, NH_4NO_3 and $FeC_2O_4.2H_2O$ [2] have also been reported. Miller [3] has reported an extensive TMA study of polymers mainly in the context of the determination of glass transitions. Other applied applications of TMA include studies of the heat-seal characteristics of polyethylene film [4], quality control of brake linings [5], characterisation of PVC plastisols [6] and the linear expansion coefficients of epoxy-resins [7].

A comprehensive review of thermomechanical methods - the relevant instrumentation and selected applications exists in the form of summaries of papers presented at a Symposium organised by the Thermal Methods Group (U.K.) in 1980 [8]. This paper further illustrates the diversity of TMA applications.

Experimental

All measurements were obtained using a Stanton Redcroft Thermomechanical Analysis System (TMA 792) with an effective operative temperature range of ambient to 1000°. Where appropriate, samples were examined in a dry dynamic nitrogen atmosphere using a flow rate of 50 cm^3 min^{-1}. Samples were contained in 5.0 x 5.2 mm platinum crucibles and covered with a 4.0 mm diameter platinum lid. Usually 50 mg sample masses were employed. Applied load, heating rate, TMA sensitivity and chart speed varied according to the sample involved but a uniform sample presentation method was applied throughout. The sample was evenly packed in the crucible, the lid applied and the system pressed at a 1.0 tonne external applied pressure. A 5 mm diameter, flat tipped quartz probe was used throughout and the platinum lid of the sample crucible effectively prevented contamination of probe by sample.

Temperature calibration of the TMA system over the range ambient - 1000° was achieved using pure metals.

Indium and potassium chromate were ICTA-DTA Certified Reference Materials [9], the other compounds used were the purest available commercial samples. The coal sample used was the U.K. National Coal Standard - identified 'High'.

Result and discussion

The temperature calibration data for the TMA system used, based on the melting transition of the metals indium, tin, zinc, aluminium and silver, are

Table 1 Calibration of a Stanton-Redcroft TMA 792 system using pure metals

Metal	M. P. (°C) (Extrapolated Onset)	M. P. (°C) Rossini[a]	Correction (°C)
Indium	159.6±0.2	156.63	-3.0
Tin	236.6±0.1	231.97	-4.6
Zinc	423.5±0.1	419.58	-3.9
Aluminium	664.0±1.7	660.37	-3.6
Silver	980.8±1.3	961.93	-18.9

a From Reference 10

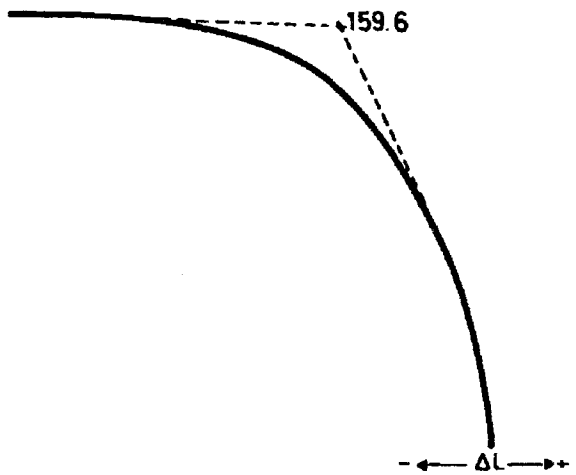

Fig. 1 TMA Indium metal : sample mass 20.6 mg : atmos. N_2 : load 10 g : heating rate 3^0 min^{-1} : TMA sensitivity 100 μm FSD : chart speed 20 mm min^{-1}

recorded in Table 1. Temperature corrections are obtained from the line of 'best fit' for the 'extrapolated onset' temperature corresponding to the melting transition as determined by TMA (y) and the best available literature melting point, [10] (x). For the system employed in the present study the temperature calibration data correspond with $y = 1.0166\ x\ -1.2491$. To il-

lustrate the procedure, the TMA profile for indium metal is shown in Fig. 1. Melting is revealed as a broad penetration drift with a corresponding extrapolated onset of 159.6°. The melting point of indium is 156.63° [10] and hence a correction of -3.0° has to be applied.

Temperatures corresponding to phase changes for the various compounds studied are quoted as 'corrected' extrapolated onset temperatures. Thermal decomposition ranges are defined by the corresponding 'corrected' extrapolated onset and offset temperatures.

Potassium Chromate

The TMA profile for K_2CrO_4 is shown in Fig. 2. A solid state phase change is revealed as a sharp expansion drift with a corresponding extrapolated onset of 671.0°. The accepted ICTA temperature for this phase change is 665 ± 7° [11].

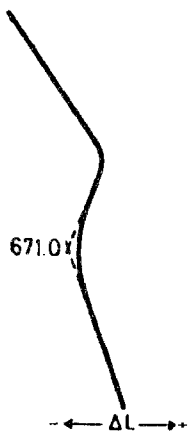

Fig. 2 TMA Potassium chromate : sample mass 50.4 mg : atmos. N_2 : load 10 g : heating rate 3° min^{-1} : TMA sensitivity 100 μm FSD : chart speed 20 mm min^{-1}

Caesium Chromate

The TMA profile for Cs_2CrO_4 is shown in Fig. 3. A solid state phase change is revealed as a sharp penetration drift with a corresponding extrapolated onset of 406.5° and a second as a sharp expansion drift with an extrapolated onset of 766.0°. Melting is revealed as a broad penetration drift with an extrapolated onset of 923.0°.

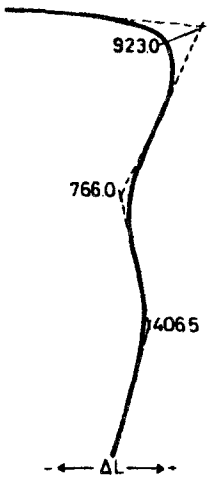

Fig. 3 TMA Caesium chromate : sample mass 50.6 mg : atmos. N_2 : load 10 g : heating rate 15° min^{-1} : TMA sensitivity 200 μm FSD : chart speed 5 mm min^{-1}

Calcium Oxalate Monohydrate

The TMA profile for $CaC_2O_4.H_2O$ is shown in Fig. 4. A three-step decomposition profile is revealed - an expansion drift and two penetration

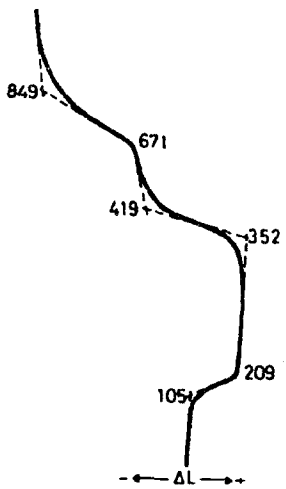

Fig. 4 TMA Calcium oxalate monohydrate : sample mass 50.4 mg : atmos. N_2 : load 50 g : heating rate 15° min^{-1} : TMA sensitivity 1000 μm FSD : chart speed 5 mm min^{-1}

drifts. The corresponding temperature ranges are 105-209°, 352-419° and 671-849° respectively. In static air, the temperature ranges, as derived by TG/DTA [12], corresponding to the loss of H_2O, CO and CO_2 are 100-226°, 346-420° and 660-840° respectively.

Copper Sulfate Pentahydrate

The TMA profile for $CuSO_4.5H_2O$ is shown in Fig. 5. A four-step decomposition profile is revealed - four penetration drifts. The corresponding

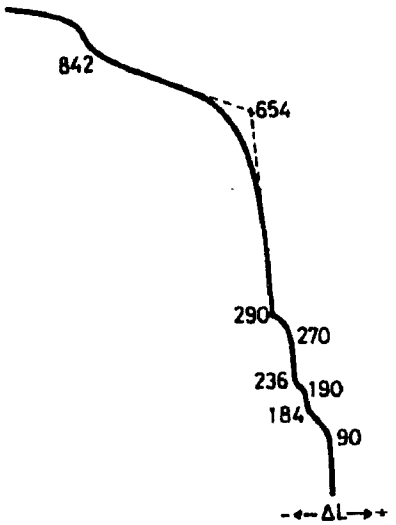

Fig. 5 TMA Copper sulfate pentahydrate : sample mass 50.3 mg : atmos. static air : load 20 g : heating rate 15° min^{-1} : TMA sensitivity 500 μm FSD : chart speed 5 mm min^{-1}

temperature ranges are 90-184°, 190-236°, 270-290° and 654-842°.

The corresponding temperature ranges as derived by TG/DTA [12] are:

100-190° ($-2H_2O$): 190-240° ($-2H_2O$): 280-340° ($-H_2O$) and 660-840° ($CuSO_4 \rightarrow CuO + SO2 + 1/2O2$).

Tungsten (powder)

The TMA profile for W is shown in Fig. 6. Tungsten is common component of pyrotechnic mixtures and the temperature range corresponding to the complete oxidation to tungsten VI oxide is of great significance in the

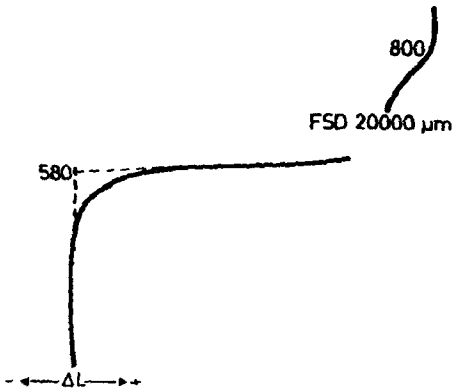

Fig. 6 TMA Tungsten (powder) : sample mass 50.3 mg : atmos. static air : load 1 g : heating rate 20° min^{-1} : TMA sensitivity 200 μm FSD : chart speed 5 mm min^{-1}

rationalisation of the energetics of these materials. Oxidation is shown as a very sharp expansion drift over the temperature range 580-800°.

Coal

TMA profile for Coal (NCB, 'High') is shown in Fig. 7. A series of softening and swelling peaks are revealed at 510, 534 and 636°. These peaks, in

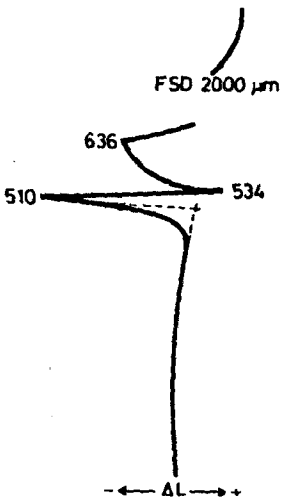

Fig. 7 TMA Coal (NCB High) : sample mass 10.6 mg : atmos. N_2 : load 1 g : heating rate 50° min^{-1} : TMA sensitivity 500 μm FSD : chart speed 5 mm min^{-1}

conjunction with the overall profile, provide a 'fingerprint' of the coal sample and the quantitative expansion and contraction data give swelling indices - these parameters are of great significance in understanding the chemical properties of coals.

Conclusion

The diversity of application of TMA has been very effectively illustrated. However, in most cases, transition temperatures different from those identified by DTA or DSC for corresponding compounds are indicated. This phenomenon is partially explained by:

a) in TMA, the site of sample temperature determination is different from that in DTA and DSC - the sample temperature thermocouple is not in direct contact with the sample thereby introducing temperature-lag phenomena.

b) the sample 'geometry' in TMA is different from that in DTA and DSC. The form of the TMA profile for each of the compounds investigated, as relating to compression or expansion transitions, is of intrinsic physical and chemical significance.

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Zusammenfassung - Der Verlauf von TG- und DTA-Kurven von solchen Verbindungen wie Calciumoxalat-Monohydrat oder Kupfersulfat-Pentahydrat sind wohlbekannt. Es wird eine TMA-Untersuchung dieser und anderer Verbindungen vorgestellt, was außer der Ermittlung interessanter Angaben über die physikalische Natur von Phasenumwandlungen und Zersetzungstemperaturintervallen auch die Einstufung des TMA-Verfahrens als ein prinzipielles thermoanalytisches Verfahren bekräftigt.