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Studies on the ageing of a magnesium–potassium nitrate pyrotechnic composition using isothermal heat flow calorimetry and thermal analysis techniques[☆]

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Abstract

The ageing behaviour of a pyrotechnic mixture of magnesium and potassium nitrate has been followed at 50 °C and 65% relative humidity by isothermal heat flow calorimetry. Measurements have been carried out with samples in air and in an inert atmosphere. The main reaction product was found to be magnesium hydroxide. This has been determined quantitatively by thermogravimetry and the amount formed correlated with the measured cumulative heat of ageing. The results have been compared with those obtained for magnesium powder studied under the same conditions. In addition the influence of the ageing process on the pyrotechnic reaction has been studied by high temperature differential scanning calorimetry under ignition conditions and modulated temperature differential scanning calorimetry.

Keywords: Ageing; Heat flow calorimetry; Magnesium; Potassium nitrate; Pyrotechnics

1. Introduction

Thermal techniques provide powerful methods for following the ageing processes in pyrotechnic compositions. These compositions are based typically on finely divided mixtures of metallic or non-metallic elements with inorganic oxidising agents [1]. The ageing behaviour of a pyrotechnic composition relates to the slow changes that can occur during storage. Such changes can have a detrimental effect on the combustion properties of the composition. Often this can be linked to the consumption of the components of the mixture or to the production of a particular product. Alternatively it may be changes in the physical or mechanical properties of the composition which result in poor performance or even in combustion failure.

In our work, where samples have been aged at temperatures in the range 40–70 °C and relative humidities (RH) from 51 to 100%, we have adopted two approaches. In one, the indirect approach, the samples are aged in a humidity cabinet for different times and then characterised by thermal analysis and calorimetric techniques. A recent example of this method is a study of the boron–potassium dichromate pyrotechnic delay system, where the ageing has been followed by high temperature differential scanning calorimetry

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under ignition conditions, time to ignition measurements and isothermal microcalorimetry [2]. It is also possible to perform pyrotechnic tests, such as burning rate, light output and exothermicity measurements on the aged compositions.

In the other approach, the samples are aged in an isothermal microcalorimeter. This enables the ageing process to be monitored directly since the technique is sufficiently sensitive to measure the small amount of heat released during ageing. The aged products can then be characterised by thermal and analytical techniques but since the sample masses are normally in the range 100–500 mg, there is insufficient material for the standard pyrotechnic tests.

In the present paper, preliminary results are reported for the ageing of the magnesium–potassium nitrate pyrotechnic system in the presence of water vapour using isothermal microcalorimetry. Previous work on this system has been carried out by Spasojevi et al. [3] using the indirect approach. Samples were aged at 85% RH in the temperature range 65–85 °C and FTIR used to follow the formation of $Mg(OH)_2$ and KNO_2.

Our own work has been carried out at 50 °C and 65% RH which is below the deliquescence point of potassium nitrate. We have compared our results with those obtained for magnesium powder under the same conditions. Since magnesium hydroxide is the main product of ageing, a method has been developed using thermogravimetry (TG) to enable the amount formed to be determined quantitatively. These studies have been supplemented by examination of the aged samples by high temperature differential scanning calorimetry (DSC) under ignition conditions and modulated temperature DSC (MTDSC). We have reported previously a preliminary study on the magnesium–sodium nitrate system [4].

2. Experimental

The studies have been carried out on a magnesium–potassium nitrate pyrotechnic composition containing equal masses of the components. The potassium nitrate was to Interim DEF STAN 68-63/1 and the Grade 4 magnesium to DEF STAN 13-130/1. The composition was prepared by blending the components in a Turbula mixer.

Microcalorimetric measurements were performed on 100 mg samples at 50 °C and 65% RH using a Thermometric Model 2277 Thermal Activity Monitor (TAM). The samples were sealed into 3 cm^3 glass ampoules. The humidity was maintained using a saturated solution of potassium iodide in a small tube in the ampoule. Samples of the residues were analysed for magnesium hydroxide by thermogravimetry and characterised by high temperature DSC under ignition conditions and MTDSC.

Thermogravimetry was carried out using a Stanton Redcroft TG1000 thermobalance. A method was devised for determining magnesium hydroxide by heating a 10 mg sample in a platinum crucible in an atmosphere of argon according to the following programme:

[a] The temperature was maintained at 25 °C for 10 min to establish the initial mass reading.
[b] The temperature was raised to 150 °C at 30 °C min^{-1} and held constant for 10 min.
[c] The temperature was raised to 320 °C at 30 °C min^{-1} and held constant for 30 min.

Magnesium hydroxide was determined from the mass loss accompanying the dehydration reaction in step [c]. The mass change in step [b] enabled the amount of moisture present in the sample to be determined. Measurements by simultaneous TG-mass spectrometry established that potassium nitrate did not decompose or react with magnesium in the temperature region of the decomposition of magnesium hydroxide.

High temperature DSC under ignition conditions was carried out using a specially developed apparatus [5]. Measurements were made on 10 mg samples, which were heated in argon at 50 °C min^{-1}. MTDSC experiments were performed using a TA Instruments Model 2920. The measurements were made on 5 mg samples contained in platinum crucibles in an atmosphere of helium with an underlying heating rate of 3 °C min^{-1}, a period of 30 s and an amplitude of 0.1 °C [6].

3. Results and discussion

3.1. Microcalorimetric studies

3.1.1. Magnesium powder

Typical heat flow and cumulative heat curves for the magnesium sample are shown in Fig. 1. It can be

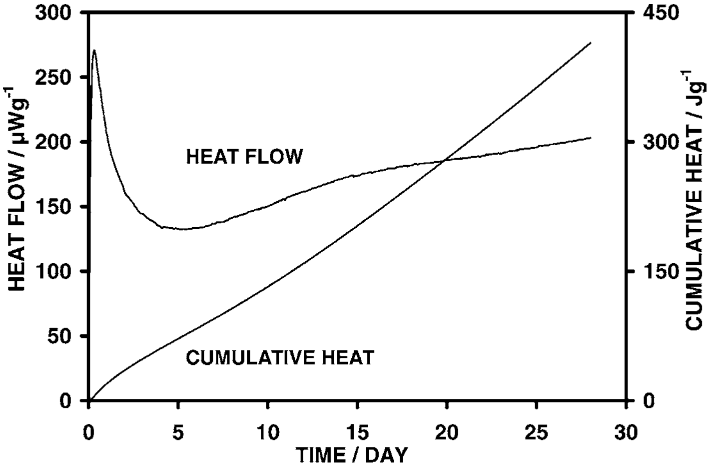

Fig. 1. Heat flow calorimetry curves for magnesium (sample mass, 100 mg; 50 °C; 65% RH; atmosphere, air).

seen that following a rapid rise to give a peak after 0.3 days, the heat flow decreased to a minimum after about 5.5 days. The signal then increased slowly for the remainder of the experiment.

The possible role of oxygen in the ageing process was assessed by carrying out experiments on samples sealed in ampoules under an atmosphere of argon. No significant differences were found from the results obtained in air. This indicates that under these closed conditions the ageing of magnesium is due to the reaction with water vapour alone. X-ray diffraction studies showed that magnesium hydroxide was the main product of the ageing reaction. This was measured quantitatively using the thermogravimetric method already described. A typical experimental curve is shown in Fig. 2. The magnesium hydroxide contents were determined from the TG curve after the application of a small buoyancy correction.

The results of duplicate TG measurements on the residues from two calorimetric experiments after 28 days are shown in Table 1. It can be seen that there is good reproducibility between the individual duplicate

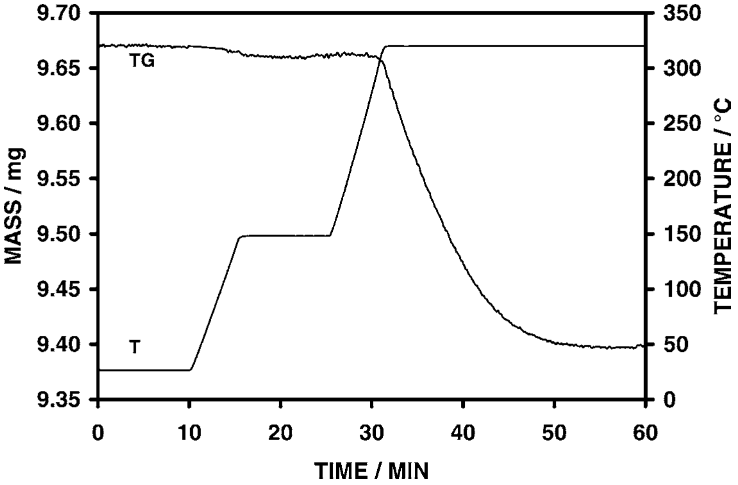

Fig. 2. Thermogravimetric method for determination of magnesium hydroxide content (sample mass, 10 mg; heating rate, 30 °C min^{-1}; atmosphere, argon).

measurements. The cumulative heats are also given in the Table 1. The similarity between the heats, together with the closeness of the TG measurements, indicates that a similar amount of ageing had taken place in the two calorimetric experiments.

Further determinations of magnesium hydroxide were carried out on samples aged in the TAM for periods ranging from 3.5 to 14 days. The amount of magnesium hydroxide formed is plotted against the time of ageing in Fig. 3. Also included are the results from the 28 days experiments. The results show that the magnesium hydroxide content increased in a

Table 1
TG Determination of magnesium hydroxide content of magnesium powder aged in air for 28 days at 50 °C and 65% RH

Experiment	Mass loss (%)	$Mg(OH)_2$ (%)	Heat ($J\,g^{-1}$)
1	2.74 2.73	8.88 8.84	415
2	2.64 2.68	8.54 8.69	410
Mean	2.70 ± 0.05	8.74 ± 0.15	413 ± 3

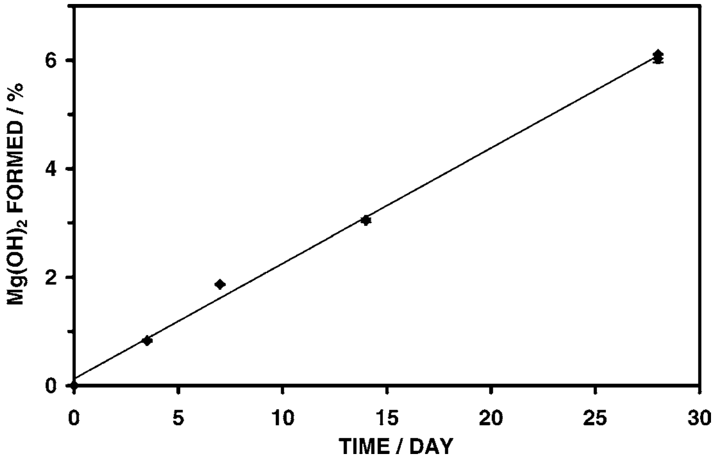

Fig. 3. Plot of $Mg(OH)_2$ formed against time of ageing for magnesium samples in air at 50 °C and 65% RH.

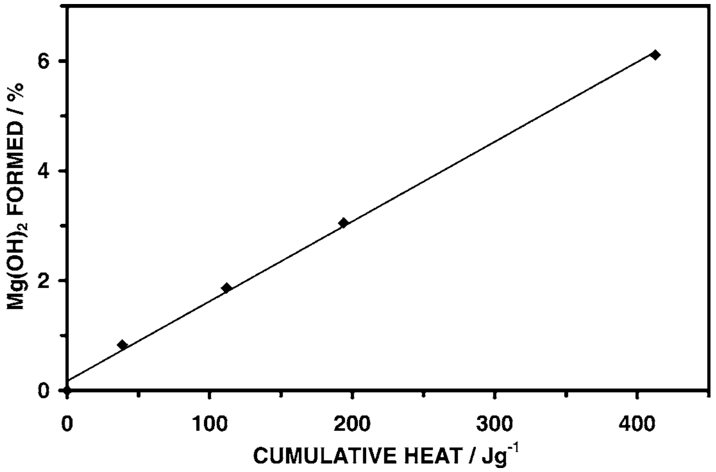

Fig. 4. Plot of $Mg(OH)_2$ formed against cumulative heat for magnesium samples aged in air at 50 °C and 65% RH.

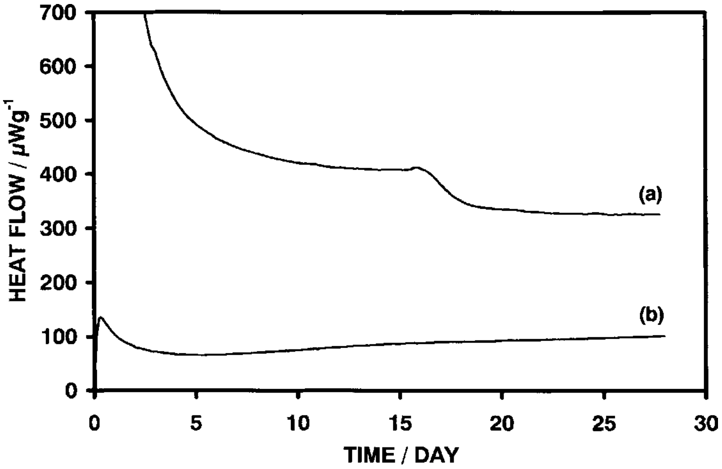

Fig. 5. Heat flow curves for (a) a 50% Mg–50% KNO_3 Composition and (b) magnesium (0.5×) (sample mass, 100 mg; 50 °C; 65% RH; atmosphere, air).

linear manner with the time of ageing. Measurements on the unaged sample showed that this already contained a significant amount of magnesium hydroxide (2.8%).

The amount of magnesium hydroxide formed is plotted against the cumulative heat in Fig. 4. The increase in the amount of magnesium hydroxide with time of ageing correlates well with the corresponding increase in the cumulative heat. The results point to the reaction,

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

being the major component of the ageing process.

3.1.2. 50% Mg–50% KNO_3 composition

The heat flow and cumulative heat flow curves obtained by microcalorimetric studies on the 50% Mg–50% KNO_3 composition over a 28 days period are shown in Figs. 5 and 6, respectively. The curves are compared with those for the same amount of

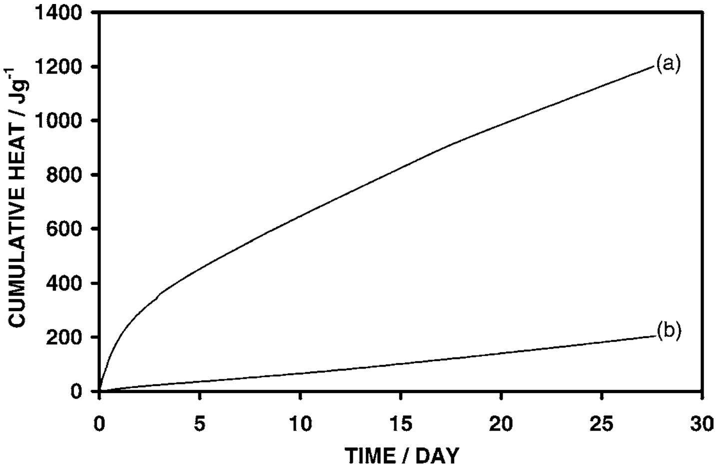

Fig. 6. Cumulative heat curves for (a) a 50% Mg–50% KNO_3 composition and (b) magnesium (0.5×) (sample mass, 100 mg; 50 °C; 65% RH; atmosphere, air).

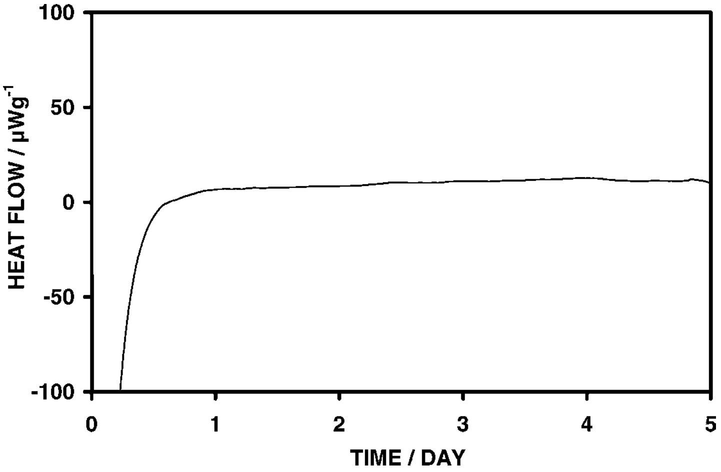

Fig. 7. Heat flow curve for potassium nitrate (sample mass, 100 mg; 50 °C; 65% RH; atmosphere, air).

magnesium as present in the composition. It can be seen that the heat flow from the pyrotechnic composition is markedly greater than that given by the magnesium alone. This is particularly significant in the initial stages of ageing. Calorimetric experiments with potassium nitrate alone in the presence of water vapour gave a negligible heat output (Fig. 7). It is therefore clear that the ageing process in the composition in the presence of water vapour must involve interaction between magnesium and potassium nitrate. Experiments with samples in argon showed a 15% reduction in the cumulative heat measured over 28 days (Fig. 8), thus indicating that aerial oxygen plays a part in the ageing process in contrast to the observations with magnesium alone.

X-ray diffraction and FTIR studies confirmed that magnesium hydroxide was the main product formed in the ageing process. FTIR measurements also appeared to indicate the presence of a small amount of nitrite. In order to follow quantitatively the amount of magnesium hydroxide formed as a function of time, a series of microcalorimetric experiments was carried

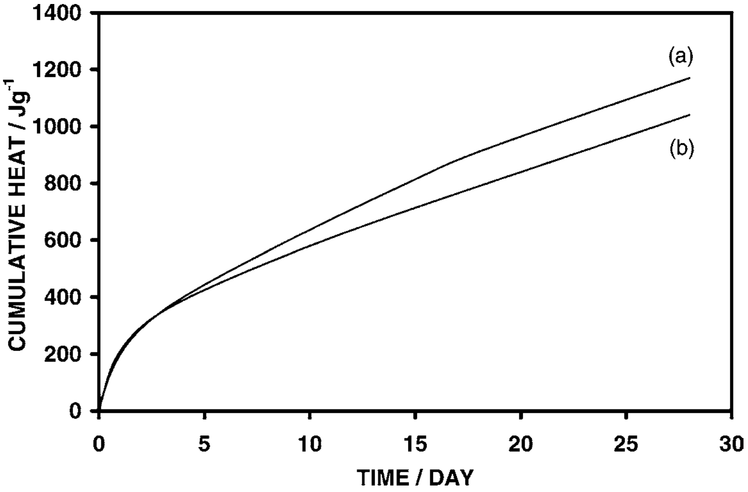

Fig. 8. Comparison of cumulative heat curves for a 50% Mg–50% KNO_3 composition (a) in air and (b) in argon (sample mass, 100 mg; 50 °C; 65% RH).

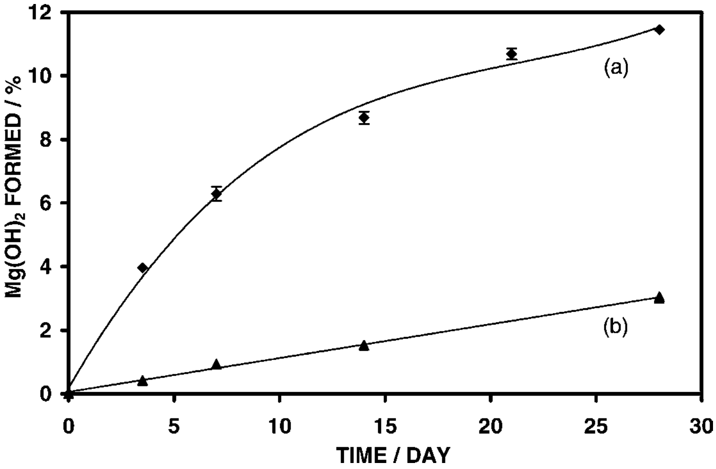

Fig. 9. Plot of $Mg(OH)_2$ formed against time of ageing in air at 50 °C and 65% RH for (a) a 50% Mg–50% KNO_3 composition and (b) magnesium (0.5×).

out to age the pyrotechnic composition for time periods ranging from 3.5 to 21 days.

The amount of magnesium hydroxide formed is plotted against the time of ageing in Fig. 9, together with the results obtained after 28 days. Also shown is the amount of magnesium hydroxide formed by the equivalent amount of magnesium. The quantity of magnesium hydroxide given by the pyrotechnic composition is markedly greater than that formed by magnesium alone and this difference is particularly significant in the initial stages of ageing. This reflects the increased heat observed for the pyrotechnic system compared with that for magnesium.

There is a good correlation between the amount of magnesium hydroxide formed and the heat evolved from the Mg–KNO_3 composition (Fig. 10). The amounts of magnesium hydroxide found are considerably greater than those measured by Spasojevi et al. [3] after ageing at 65 °C, in spite of the higher humidity used by these authors [3]. However, the experimental conditions adopted by Spasojevi et al. were different to those used in the present work and

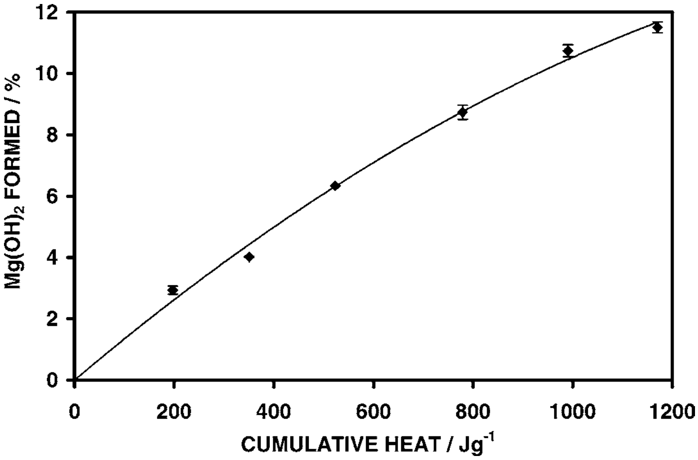

Fig. 10. Plot of $Mg(OH)_2$ formed against cumulative heat for a 50% Mg–50% KNO_3 composition aged in air at 50 °C and 65% RH.

Table 2
Ignition temperatures determined by DSC for a 50% Mg–50% KNO_3 composition aged in air for different times at 50 °C and 65% RH

Age (days)	Ignition temperature (°C)
0	627 ± 3
1	633 ± 0
2	639 ± 1
3	643 ± 1
5	647 ± 1
7	645 ± 1
14	645 ± 1

DSC conditions: sample mass, 10 mg; heating rate, 50 °C min^{-1}; atmosphere, argon.

the type of magnesium was not specified which makes comparison difficult.

3.2. High temperature DSC studies

High temperature DSC studies were carried out under ignition conditions to investigate the influence of the ageing process on the high temperature pyrotechnic reaction. The ignition temperature of samples aged from 1 to 14 days is shown in Table 2. The values increased rapidly over the first 5 days of ageing and then remained unchanged on further ageing. The DSC curves for the compositions aged for 1 and 2 days (Fig. 11) show that the pre-ignition exothermic reaction given by the unaged composition was significantly reduced after only 1 day of ageing. The proximity of the ignition temperature after 5 days of ageing to the melting temperature of magnesium (650 °C) suggests that fusion of unreacted magnesium may be the trigger for ignition in these compositions.

3.3. Modulated temperature DSC studies

MTDSC has been shown to have a number of advantages over conventional DSC in the study of pyrotechnic systems [6]. The resolution of the normal DSC signal into the reversing and non-reversing components enables the fusion behaviour of the oxidant to be observed even in the presence of the highly exothermic reaction between the oxidant and the fuel.

In the present work, MTDSC measurements showed that the pre-ignition reaction in the 50% Mg–50% KNO_3 composition started at about 330 °C. This is in the region of the fusion of potassium nitrate, which is shown by a sharp endothermic peak. The influence of ageing is clearly demonstrated in Fig. 12, where the total heat flow signal after ageing for just 1 day shows no sign of this low temperature pre-ignition reaction. A comparison between the reversing signals for unaged and aged samples shows that ageing for 1 day produces a broader melting peak with a reduced melting temperature. The endotherm at 275 °C observed in the total heat flow signal for the aged composition, is due to the decomposition of magnesium hydroxide and hence does not appear in the reversing signal.

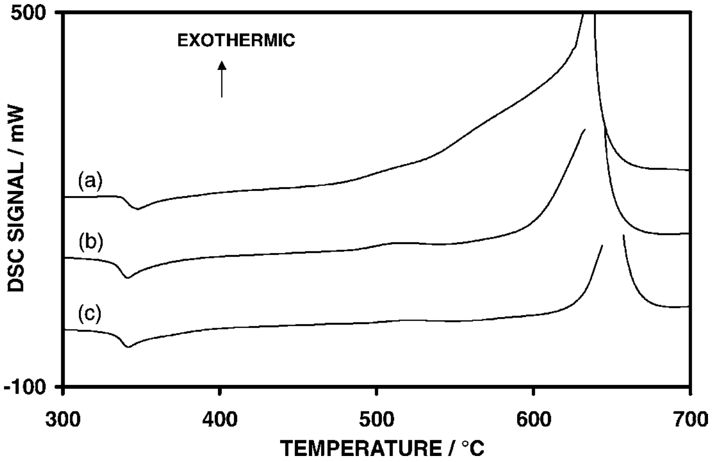

Fig. 11. DSC curves for a 50% Mg–50% KNO_3 composition (a) unaged and aged for (b) 1 and (c) 2 days in air at 50 °C and 65% RH (sample mass, 10 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

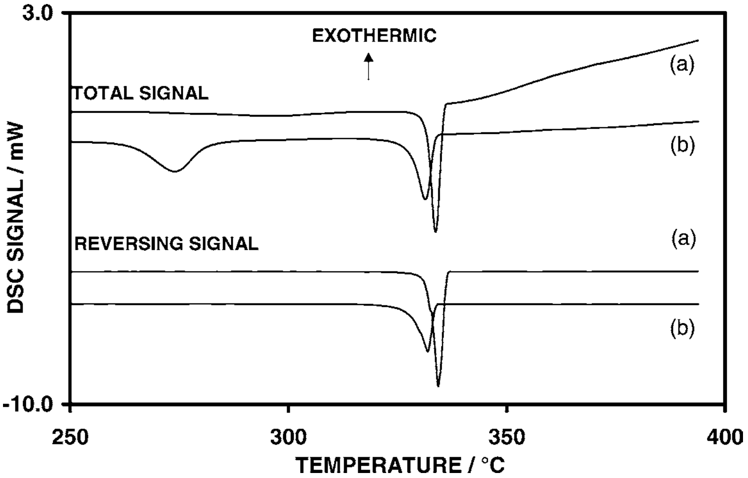

Fig. 12. MTDSC curves for a 50% Mg–50% KNO_3 composition (a) unaged and (b) aged in air at 50 °C and 65% RH for 1 day (sample mass, 5 mg; heating rate, 3 °C min^{-1}; atmosphere, helium; period, 30 s; amplitude, 0.1 °C).

4. Conclusions

Microcalorimetric studies of the ageing of 50% Mg–50% KNO_3 in air at 50 °C and 65% RH have shown that potassium nitrate plays an essential role in the increased rate of ageing compared with that of magnesium alone. The major product of ageing is magnesium hydroxide and a good correlation has been found between the heat evolved in the ageing process and the amount of magnesium hydroxide formed. High temperature DSC and MTDSC studies have shown that the high temperature reaction between magnesium and potassium nitrate is affected directly by the ageing process at 50 °C and 65% RH.

Work is in progress to make additional quantitative measurements of the components of aged samples including total magnesium, nitrate and nitrite contents. In addition, a technique has been developed for free magnesium determination with samples in the mass range 10–20 mg. It is hoped that these methods, in conjunction with the thermal studies, will provide a better insight into the ageing process of the magnesium–potassium nitrate system and other nitrate-based pyrotechnic compositions.

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