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Studies on the ageing of a magnesium–strontium nitrate pyrotechnic composition using isothermal microcalorimetry and thermal analysis techniques

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Abstract

The ageing behaviour of a pyrotechnic composition containing equal parts by mass of magnesium and strontium nitrate has been followed by isothermal microcalorimetry. The measurements were carried out on the samples at 50 °C and 65% relative humidity in air using closed ampoules. The results have been compared to those obtained for magnesium powder under the same conditions. Following an initial induction period, the pyrotechnic compositions reacted at a much faster rate than magnesium powder alone. The main reaction products were found to be magnesium hydroxide and strontium nitrite; the amounts formed have been correlated with the cumulative heats of ageing. In addition, the influence of the ageing process on the pyrotechnic reaction has been studied by high temperature differential scanning calorimetry (DSC) and by modulated temperature DSC.

Keywords: Ageing; DSC; Isothermal microcalorimetry; Magnesium; Pyrotechnics; Strontium nitrate; Thermal analysis

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1. Introduction

Pyrotechnic compositions are used in a wide range of applications to produce light, heat, sound and smoke [1]. Those employed to generate light usually contain magnesium powder and an inorganic oxidant. The amount of light emitted and the rate of burning of the composition can be controlled by changing the magnesium to oxidant ratio, the particle size of the components or by the addition of a binder.

In the powdered form pyrotechnic compositions can be used to produce a rapid and very intense pulse of light, but for most applications the compositions are consolidated into a paper or metal tube under high pressure. The flares produced by this process burn with an essentially constant light output and are used for signalling and area illumination. Their burning times can range from a few seconds up to several minutes depending on the application. Fast burning magnesium–strontium nitrate compositions are also used as tracers. The tracer allows the trajectory of ammunition to be observed during flight and is used to determine the correction to be applied to the aim of a weapon system.

All pyrotechnic compositions containing magnesium degrade during storage, this changes the performance of the composition and ultimately can result in the composition failing to function. As discussed previously [2], we are using two approaches to study the ageing of pyrotechnic compositions. In the indirect approach the samples are aged in a humidity cabinet, typically at 50 °C and at a relative humidity (RH) in the range 65–74%. They are then studied by thermal and analytical techniques. In the other approach, ageing is followed directly by isothermal microcalorimetry, which is sufficiently sensitive to measure the small amount of heat released during the ageing process. Characterisation of the aged compositions enables a thermal property, such as ignition temperature, or the amount of a product formed

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to be correlated directly with the heat of ageing. However, since the sample masses used in the microcalorimeter are normally in the range 100–500 mg, there is insufficient material for the standard pyrotechnic tests including burning rate and light output measurements. This approach has been reported in a recent study on the magnesium–potassium nitrate system [2] and has been used in a preliminary study on the magnesium-sodium nitrate system [3].

The magnesium–strontium nitrate system does not seem to have been studied previously by isothermal microcalorimetry. Barišin and co-workers [4–7], using the indirect approach, have investigated magnesium–strontium nitrate compositions that also contained potassium perchlorate, an aluminium–magnesium alloy and a phenolformaldehyde resin binder. The samples were aged in hermetically sealed containers and the desired humidity was obtained using sulphuric acid. The majority of the studies were carried out at 75 °C and relative humidities of 78, 85 and 98.5%. Analysis of the aged products by IR spectroscopy and X-ray diffraction revealed the formation of magnesium hydroxide, strontium carbonate and strontium nitrite.

The present paper reports the results of an ageing study on a binary magnesium–strontium nitrate pyrotechnic composition containing equal parts by mass of the components. Isothermal microcalorimetry measurements were performed on the samples at 50 °C and 65% RH in air using closed glass ampoules. Thermal analysis studies have been carried out on the aged samples in order to evaluate the influence of the ageing process on the reactions taking place at higher temperatures. These have included high temperature differential scanning calorimetry (DSC) under both ignition and non-ignition conditions and an investigation of the pre-ignition reaction by modulated temperature DSC (MTDSC).

2. Experimental

Studies have been carried out on a binary composition containing equal proportions by mass of Grade 4 cut magnesium to UK MOD Defence Standard 13-130/1 and strontium nitrate to UK MOD Defence Standard 68-40/2. The strontium nitrate was dried at 80 °C and passed through a 125 μm sieve before use. 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. 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. The experiments were carried out for periods of up to 28 days and the heat flow from the samples was monitored continuously throughout the ageing period. In addition, a limited number of experiments were performed at 69% RH which was obtained using a saturated solution of sodium nitrate.

Samples of the aged compositions were analysed for magnesium hydroxide content by thermogravimetry (TG) using a modified version of the method described previously for studies on magnesium and the magnesium–potassium nitrate system [2]. The measurements were performed using a Stanton Redcroft TG1000 thermobalance with 10 mg samples, in platinum crucibles, using an argon atmosphere. The moisture content of the sample was determined by heating at 30 °C min^{-1} from ambient to 150 °C and maintaining the temperature for 10 min. The temperature was then raised to 300 °C at 10 °C min^{-1} and held for 45 min to determine the magnesium hydroxide content.

The final temperature was reduced from the value of 320 °C used previously, since preliminary studies on a composition aged for 28 days at 50 °C and 65% RH indicated that there was a slow mass loss at this temperature. The loss was attributed to the decomposition of strontium nitrite formed in the ageing process and was confirmed by simultaneous TG-mass spectrometry. This showed that a small amount of NO was evolved above 260 °C and that the rate of evolution accelerated markedly above 400 °C. In addition, the heating rate between 150 and 300 °C was reduced from 30 to 10 °C min^{-1}, since this was found to reduce the evolution of NO during the hydroxide decomposition.

The strontium nitrite content of the aged compositions was determined using a spectrophotometric method based on the diazotisation of sulphanilamide by the nitrite ion in acid solution, followed by coupling with *N*-(1-napthyl) ethylenediamine dihydrochloride. The absorbance of the resulting solution was measured at a wavelength of 550 nm.

High temperature DSC under ignition conditions was carried out using an apparatus specially modified for pyrotechnic studies [8]. Measurements were made on 20 mg samples, which were heated in 2 cm long quartz crucibles, at 50 °C min^{-1} in flowing argon. Shallow inconel crucibles containing titanium powder were placed on top of the DSC head to reduce the level of oxygen impurity in the argon. A photocell was used to detect the light emitted as the composition ignited.

Experiments were also performed on the aged samples under non-ignition conditions, using a high temperature DSC apparatus with a chromel heat flux plate. Measurements were made on 10 mg samples in quartz crucibles, at a heating rate of 10 °C min^{-1}, with an argon atmosphere.

MTDSC experiments were carried out using a TA Instruments Model 2920. The measurements were made on 5 mg samples contained in platinum crucibles using 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 [9].

3. Results and discussion

3.1. Microcalorimetry studies

Preliminary experiments on the 50% magnesium–50% strontium nitrate composition, carried out over a 3-day period at 50 °C and 65% RH in air, showed only a small heat

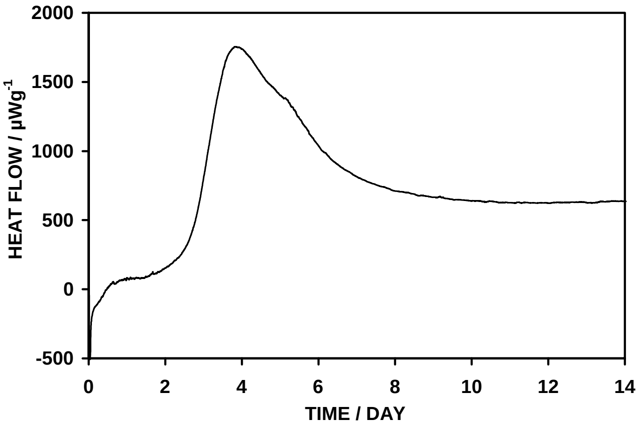

Fig. 1. Heat flow curve for a 50% Mg–50% $Sr(NO_3)_2$ composition (sample mass, 100 mg; 50 °C, 69% RH; atmosphere, air).

flow signal of about 50 µW g^{-1}. However, measurements at 69% RH gave considerably larger heat flows with maximum values in the region of 1750 µW g^{-1} and this is illustrated in Fig. 1. The heat flow curve showed an initial plateau between 1 and 2 day suggesting that there was an induction period before onset of the main reaction. This effect was not observed for either the magnesium–potassium nitrate [2] or magnesium–sodium nitrate [3] systems when they were studied at 50 °C and 65% RH.

Further experiments at 65% RH, for periods up to 28 days, revealed an extended induction period and this is illustrated by selected heat flow and cumulative heat curves in Figs. 2 and 3, respectively. The times taken to reach the peak maximum ranged from 14.9 to 24.4 days. However, the maximum heat flow values showed good reproducibility and a mean value of 1124 ± 40 µW g^{-1} was given. Apart from the experiment showing the longest induction time, the heat flow curves showed a rapid rise to the peak maximum and gave similar cumulative heats (mean value 274 ± 17 J g^{-1}) at the maximum heat flow. As in the experiments at 69% RH, the reaction was found to continue at a significant rate following the main peak.

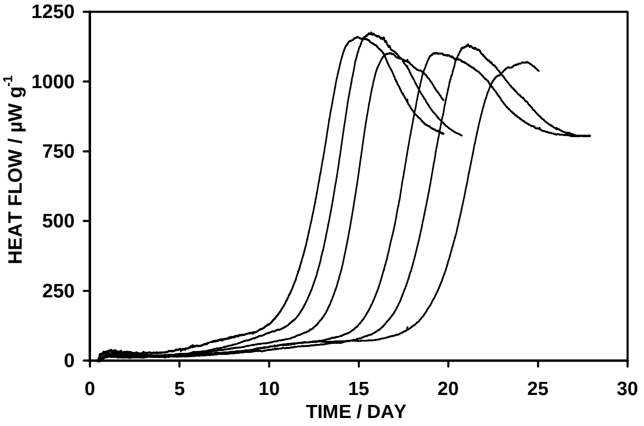

Fig. 2. Heat flow curves for a 50% Mg–50% $Sr(NO_3)_2$ composition (sample mass, 100 mg; 50 °C, 65% RH; atmosphere, air).

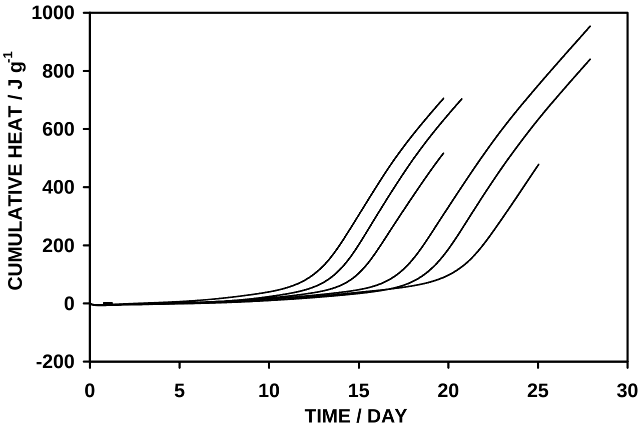

Fig. 3. Cumulative heat curves for a 50% Mg–50% $Sr(NO_3)_2$ composition (sample mass, 100 mg; 50 °C, 65% RH; atmosphere, air).

Expanded heat flow plots are given in Fig. 4. The time taken before the onset of the main reaction would appear to be related to the heat flow signal observed during this period. Thus, the samples which gave the highest initial signals also appeared to give the shortest induction times. Although it is difficult to measure precisely the onset time for the main reaction, it would appear that the cumulative heat at this point for the majority of experiments fell within a relatively narrow band ranging from 50 to 70 J g^{-1}.

The variation in times to the onset of the main reaction meant that there was no direct relationship between the time and extent of ageing. Therefore, characterisation of the aged compositions was performed on samples prepared on the basis of increasing extent of reaction. This was determined from the cumulative heat values, irrespective of the time taken to achieve the required cumulative heat, up to values in the region of 1000 J g^{-1}. In view of the limited amounts of aged sample available from each microcalorimetry measurement, sufficient experiments were performed to provide samples for both chemical analysis and thermal analysis studies.

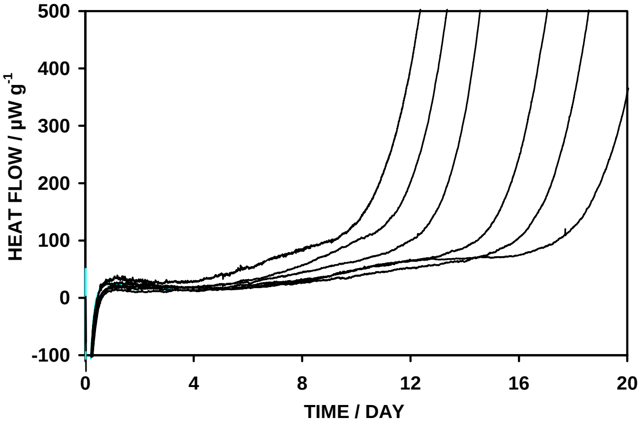

Fig. 4. Heat flow curves for a 50% Mg–50% $Sr(NO_3)_2$ composition (expanded scale) (sample mass, 100 mg; 50 °C, 65% RH; atmosphere, air).

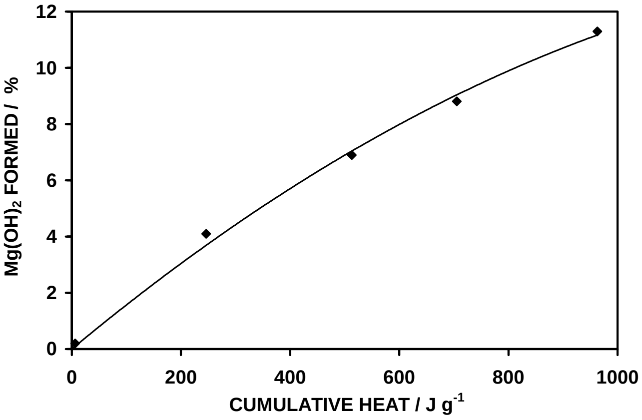

Fig. 5. Plot of $Mg(OH)_2$ formed against cumulative heat for a 50% Mg–50% $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH.

Preliminary X-ray diffraction and Fourier transform infrared spectroscopy (FTIR) studies on an aged composition showed the presence of both magnesium hydroxide and strontium nitrite. Magnesium hydroxide determinations were performed on selected compositions using the TG method described earlier. The unaged sample was found to have a hydroxide content of 1.2% and this value was subtracted from the measured hydroxide content of the aged compositions to give the amount formed during the ageing process. The amount of magnesium hydroxide formed is plotted as a function of cumulative heat in Fig. 5. The results show that in spite of the variations in the induction times there is a good correlation between the extent of reaction, as measured by the cumulative heat, and the amount of magnesium hydroxide produced.

The heat flow curve from one of the experiments on the 50% magnesium–50% strontium nitrate composition is shown in Fig. 6. This is compared with a curve obtained for the same amount of magnesium present in the composition. It can be seen that after 12 days the heat flow from the pyrotechnic composition becomes markedly greater than that given by the magnesium powder. Since a negligible heat flow signal was given by strontium nitrate under the same conditions (Fig. 6), it is clear that a major component of the ageing process in the composition must involve direct interaction between magnesium and the nitrate. A similar conclusion was reached from microcalorimetry experiments on a 50% magnesium–50% potassium nitrate composition [2].

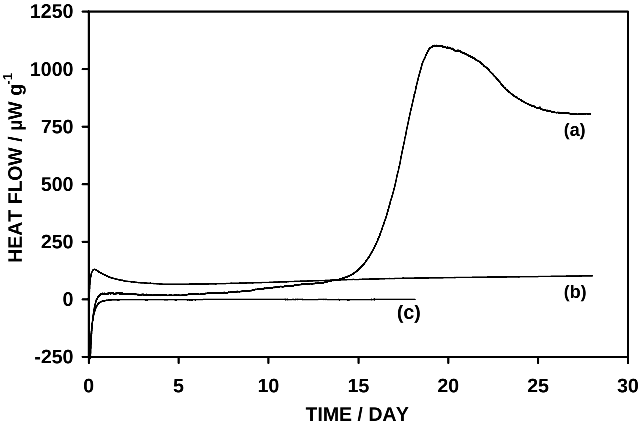

Fig. 6. Heat flow curves for: (a) a 50% Mg–50% $Sr(NO_3)_2$ composition, (b) magnesium (0.5×) and (c) $Sr(NO_3)_2$ (0.5×) (sample mass, 100 mg; 50 °C, 65% RH; atmosphere, air).

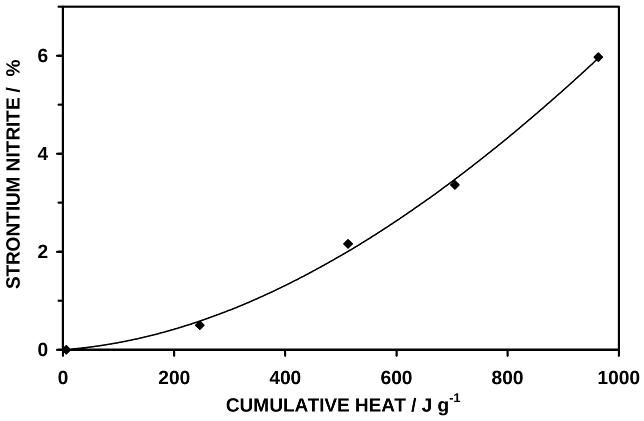

Fig. 7. Plot of strontium nitrite formed against cumulative heat for a 50% Mg–50% $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH.

The samples were also analysed for their strontium nitrite content using the spectrophotometric method described earlier. The results of the measurements are plotted as a function of cumulative heat in Fig. 7. It can be seen that only a small amount of strontium nitrite was formed in the initial stages of the ageing process. Thus, the sample aged for 16 days to give a cumulative heat of 246 J g^{-1} gave only 0.5% nitrite, but produced 4.1% magnesium hydroxide. The rate of nitrite formation increased with increasing cumulative heat and a maximum of 6.0% nitrite was observed for a heat of reaction of 963 J g^{-1}. This is in contrast to the rate of formation of magnesium hydroxide which decreased as the cumulative heat increased.

A possible route for the formation of strontium nitrite may be written:

$$2Mg + Sr(NO_3)_2 + 2H_2O \rightarrow 2Mg(OH)_2 + Sr(NO_2)_2$$

The amount of magnesium hydroxide formed due to this reaction has been calculated from the analysis results for strontium nitrite. This is plotted in Fig. 8 together with the total amount of hydroxide determined in the TG experiments and the curve reflecting the difference between the two sets of values. Work in progress on samples aged at 69% RH and 50 °C suggests that at cumulative heats in excess of 1400 J g^{-1}, the reaction involving the production of nitrite, assuming the above equation, becomes the major source for the production of magnesium hydroxide.

The results obtained in these studies cannot be compared directly with those obtained by Barišin and co-workers [4–7] due to the markedly higher humidities used in their work. Since the equilibrium relative humidity of strontium nitrate

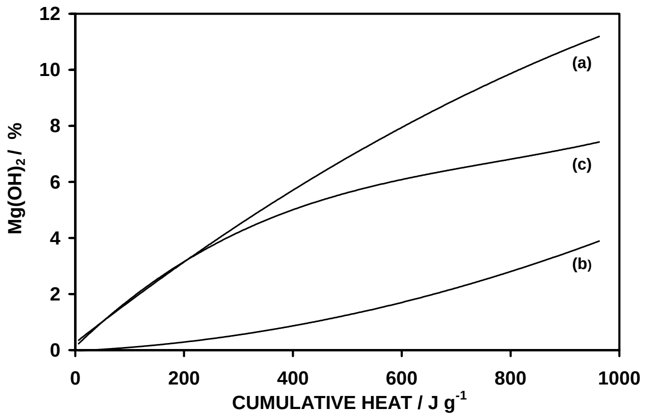

Fig. 8. Plots of magnesium hydroxide formed against cumulative heat for a 50% Mg–50% $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH: (a) measured $Mg(OH)_2$; (b) calculated $Mg(OH)_2$ produced in nitrite formation (see text); (c) difference curve.

at 25 °C is reported to be 85.1% [10], some of the studies by Barišin et al. would have been made above the deliquescence point of strontium nitrate. Indeed, in one paper, they refer to reaction in a solid–liquid system [7].

They have attributed the presence of nitrite in their aged compositions to the reduction of nitrate by hydrogen generated by the reaction of magnesium with moisture. Work in progress using a relative humidity perfusion cell to investigate the behaviour of a number of nitrates in a 5% hydrogen–95% argon mixture at 65% RH and 50 °C, indicates that strontium nitrate does not react with hydrogen under these conditions [11]. The presence of strontium carbonate as a major product of reaction in the studies of Barišin and co-workers [4–7] suggests that although they were working in a closed system, there was sufficient access of CO_2 when the vessel was opened to take out aged samples.

3.2. Differential scanning calorimetry 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; representative curves are given in Fig. 9. They reveal the presence of a pre-ignition reaction starting at about 400 °C and overlapping with the endothermic decomposition of magnesium hydroxide at around 350 °C. The magnitude of the pre-ignition reaction increased with increasing extent of ageing and this has resulted in a reduction in the measured ignition temperature compared to that of the unaged material.

The ignition temperatures are plotted as a function of cumulative heat in Fig. 10. The ignition temperature decreased linearly with increasing cumulative heat until the 700 J g^{-1} level when a value of 560 °C was given which is some 27 °C lower than the unaged composition. This reduction in the ignition temperature with increasing ageing was unexpected, since ageing would normally reduce the reactivity of a composition with a concomitant increase in the ignition temperature. For example, after ageing in air for 5 days at 50 °C and 65% RH, the ignition temperature of a 50% magnesium–50% potassium nitrate composition had increased by some 20 °C [2].

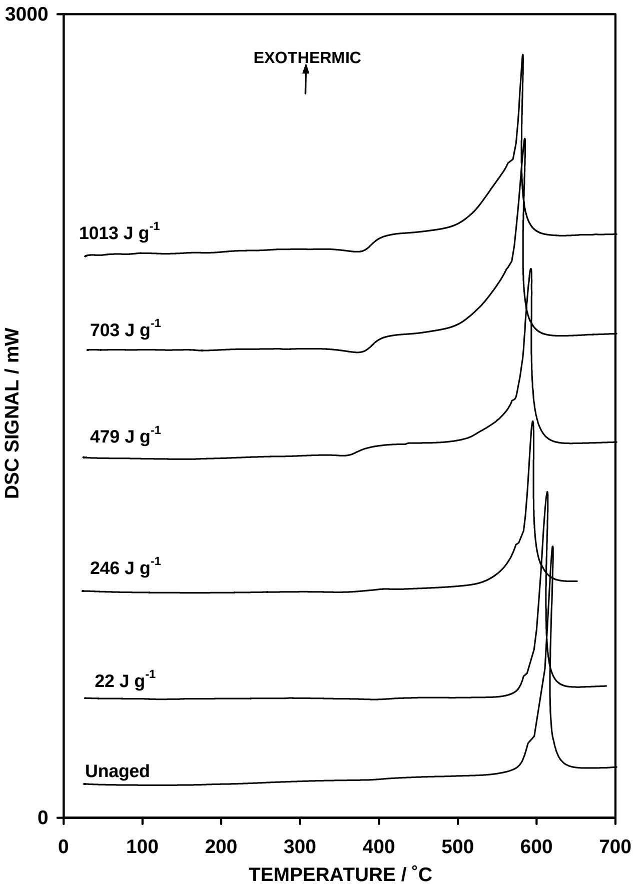

Fig. 9. DSC curves, obtained under ignition conditions, for a 50% Mg–50% $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH to different cumulative heats (sample mass, 20 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

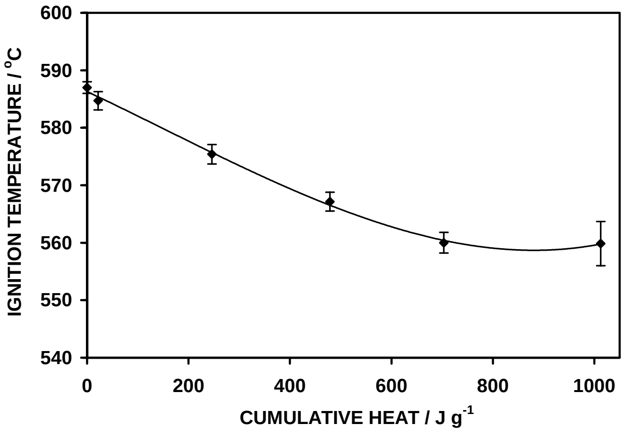

Fig. 10. Plot of ignition temperature against cumulative heat for 50% Mg–50% $Sr(NO_3)_2$ samples aged at 50 °C and 65% RH (sample mass, 20 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

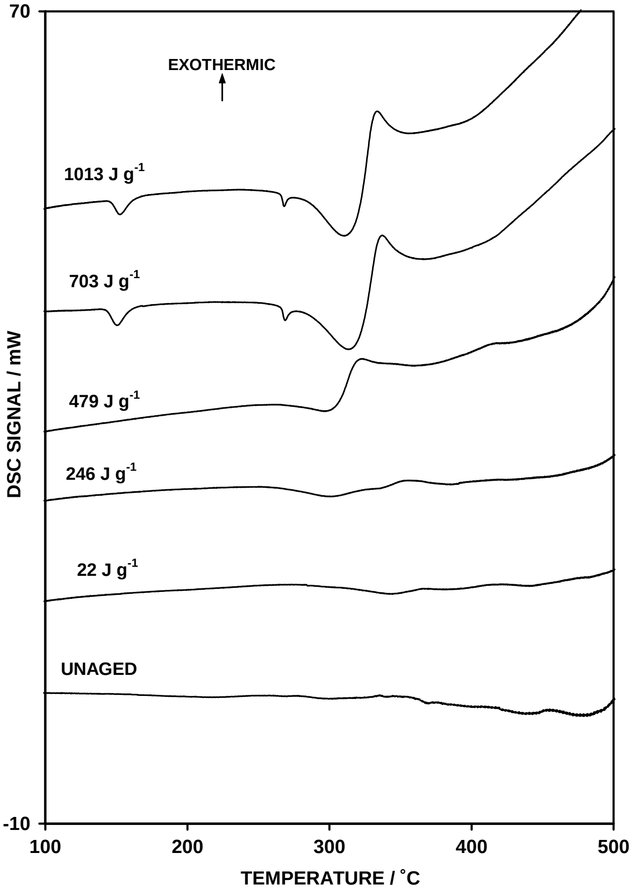

Fig. 11. DSC curves, obtained under non-ignition conditions, for a 50% Mg–50% $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH to different cumulative heats (sample mass, 10 mg; heating rate, 10 °C min^{-1}; atmosphere, argon).

The influence of ageing on the pre-ignition reaction has been studied in more detail by DSC measurements under non-ignition conditions. The curves are given in Fig. 11 and confirm that as the extent of ageing increased the amount of exothermic activity above 320 °C also increased significantly. As noted in the experiments under ignition conditions the exothermic reaction overlapped the endothermic peak at 300 °C, resulting from the decomposition of magnesium hydroxide formed in the ageing process.

The presence of a pre-ignition reaction and its enhancement with increasing extent of ageing is considered to be due to the strontium nitrite formed in the ageing process. Strontium nitrite has been reported to melt at about 360 °C and to undergo slow decomposition in this region [12]. The nitrite could therefore exhibit increased reactivity towards magnesium compared with strontium nitrate, where TG–MS studies showed that the onset of the main decomposition reaction took place above 570 °C.

The samples with cumulative heats of 703 and 1013 J g^{-1} showed a small endothermic peak at 270 °C. This is in good agreement with the reported temperature of 267 °C for the solid–solid transition in strontium nitrite [12]. The endothermic peak in the region of 150 °C is thought to be due to the loss of water of crystallisation since strontium nitrite is normally formed as the monohydrate.

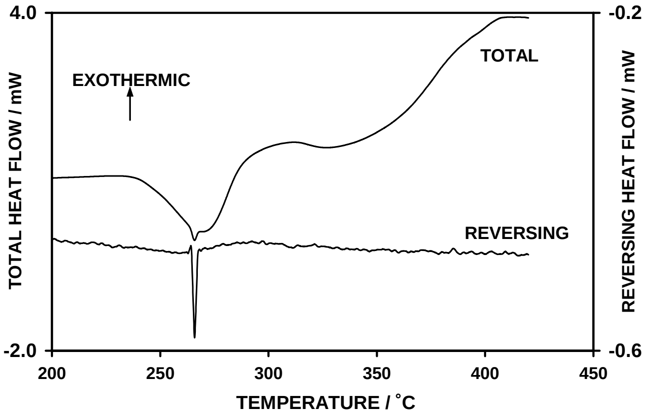

Fig. 12. MTDSC curves for a 50% Mg–50 % $Sr(NO_3)_2$ composition aged in air at 50 °C and 65% RH to a cumulative heat of 963 J g^{-1} (sample mass, 5 mg; heating rate, 3 °C min^{-1}; atmosphere, helium; amplitude, 0.1 °C; period, 30 s).

MTDSC was also used to study the pre-ignition reaction since the technique has been shown to have a number of advantages over conventional DSC in the study of pyrotechnic systems [9]. The resolution of the normal DSC signal into the reversing and non-reversing components can often enable the fusion behaviour of the oxidant to be observed even in the presence of the highly exothermic reaction between the oxidant and the fuel.

Samples aged to cumulative heat levels up to 963 J g^{-1} were studied by MTDSC over the range 200–420 °C. The presence of the solid–solid transition in strontium nitrite was detected, in the form of a sharp peak at 266 °C on the reversing signal, for samples aged to cumulative heat of 705 J g^{-1} and above. This is illustrated in Fig. 12 for the sample with the maximum cumulative heat. The transition can also be seen on the total DSC curve as a small peak superimposed on the broad endotherm given by the decomposition of magnesium hydroxide. The latter endotherm occurs at a markedly lower temperature than in the high temperature DSC experiments due to the smaller sample size and lower heating rates used in the MTDSC experiments.

The melting of the strontium nitrite was not observed by MTDSC. However, previous DTA studies with 5 mg samples of the nitrite at a heating rate of 10 °C min^{-1}, showed only a poorly defined endothermic peak [13]. This was resolved by using a faster heating rate and increased sample size to reduce the amount of nitrite decomposition, which was suppressed by the self-generated atmosphere. The conditions used for MTDSC, including the use of the highly diffusive gas helium, are unlikely to lead to a clear fusion peak for small quantities of nitrite. It is intended to synthesise strontium nitrite, which is not available commercially, to investigate further its role in the pre-ignition reaction. In addition the possibility of eutectic formation with strontium nitrate will also be studied.

4. Conclusions

Studies performed by isothermal microcalorimetry at 50 °C and 65% RH in air using closed ampoules, have enabled the ageing of a 50% magnesium–50% strontium nitrate pyrotechnic composition to be compared directly with that of magnesium powder under the same conditions. Following an initial induction period, the pyrotechnic composition was found to react at a much faster rate than magnesium alone, showing that the ageing process involves a direct reaction between strontium nitrate and magnesium in the presence of water vapour.

The major products of the ageing process were identified by X-ray diffraction and FTIR measurements as magnesium hydroxide and strontium nitrite. The amounts present have been quantified by TG and spectrophotometric methods. In view of the variable length of the induction reaction, samples for analysis were prepared on the basis of increasing cumulative heat. The measurements enabled a good correlation to be demonstrated between the heat evolved in the ageing process and the amount of magnesium hydroxide and strontium nitrite formed.

DSC studies have shown that the formation of strontium nitrite has a significant influence on the high temperature pyrotechnic reaction between magnesium and strontium nitrate. Thus, the ignition temperature of the unaged material was reduced from 587 to 560 °C after ageing to a cumulative heat value of 703 $\mathrm{J\,g^{-1}}$. This increase in reactivity is in contrast to the expected behaviour where ageing normally reduces the reactivity of a pyrotechnic system.

Work is in progress to characterise the influence of humidity and fuel:oxidant ratio on the ageing of the magnesium–strontium nitrate system. Further studies are required to establish the nature of the induction reaction. These will include additional quantitative measurements of the components of aged samples including total magnesium and nitrate 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 both the induction reaction and ageing of the magnesium–strontium nitrate system.

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References

[1] A.P. Hardt, Pyrotechnics, Pyrotechnica Publications, USA, 2001.
[2] S.D. Brown, E.L. Charsley, S.J. Goodall, T.T. Griffiths, P.G. Laye, J.J. Rooney, Thermochim. Acta 401 (2003) 53.
[3] E.L. Charsley, S.J. Goodall, T.T. Griffiths, P.G. Laye, Proceedings of the 12th Symposium on Chemical Problems Connected with the Stability of Explosives, Karlsborg, Sweden, 2001.
[4] D. Barišin, I. Batinić-Haberle, Propellants, Explos. Pyrotech. 14 (1989) 162.
[5] I. Batinić-Haberle, D. Barišin, I. Spasojevi, Proceedings of the 20th International ICT Conference, Fraunhofer-Institut, Germany, 1989, p. 61-1.
[6] D. Barišin, I. Spasojević, I. Batinić-Haberle, Proceedings of the Pyroteknikdagen, Sekt. Detonik Förbränning, Sweden, 1990, p. 145.
[7] I. Batinić-Haberle, D. Barišin, I. Spasojević, Z. Vranic, Propellants, Explos. Pyrotech. 17 (1992) 10.
[8] E.L. Charsley, S.B. Warrington, T.T. Griffiths, Proceedings of the 26th International ICT Conference, Fraunhofer-Institut, Germany, 1995, p. 23-1.
[9] E.L. Charsley, J.J. Rooney, H.A. Walker, T.T. Griffiths, T.A. Vine, B. Berger, Proceedings of the 24th International Pyrotechnics Seminar, IIT Research Institute, Chicago, USA, 1998, p. 147.
[10] L. Greenspan, J. Res. Natl. Bureau Stand. 81A (1977) 89.
[11] I. Tuukkanen, E.L. Charsley, J.J. Rooney, T.T. Griffiths, unpublished work.
[12] S.B. Warrington, P.A. Barnes, E.L. Charsley, in: D. Dollimore (Ed.), Proceedings of the 2nd European Symposium on Thermal Analysis and Calorimetry, Heyden, 1981, p. 315.
[13] S.B. Warrington, Ph.D. Thesis, Leeds Polytechnic, 1982.