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Thermochimica Acta 426 (2005) 115–121
thermochimica acta
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A study of the influence of the fuel to oxidant ratio on the ageing of magnesium–strontium nitrate pyrotechnic compositions using isothermal microcalorimetry and thermal analysis techniques

I.M. Tuukkanen[a], S.D. Brown[b], E.L. Charsley[b,*], S.J. Goodall[b], P.G. Laye[b], J.J. Rooney[b], T.T. Griffiths[c], H. Lemmetyinen[d]

[a] *Defence Forces Materiel Command, P.O. Box 69, FIN-33541, Tampere, Finland*
[b] *Centre for Thermal Studies, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK*
[c] *QinetiQ Ltd., Fort Halstead, Sevenoaks, Kent TN147BP, UK*
[d] *Institute of Materials Chemistry, Tampere University of Technology, P.O.B. 527, FIN-33101, Tampere, Finland*

Received 14 April 2004; received in revised form 21 June 2004; accepted 6 July 2004

Abstract

The influence of the fuel to oxidant ratio on the ageing behaviour of the magnesium–strontium nitrate pyrotechnic system in the presence of water vapour has been investigated by isothermal microcalorimetry in conjunction with chemical and thermal analysis measurements. The major products of ageing were identified as magnesium hydroxide and strontium nitrite. Measurement of the ratio of the amount of magnesium hydroxide formed to that of strontium nitrate reacted has shown that for compositions containing from 10 to 60% magnesium, a major component of the ageing process could be represented by the equation $3Mg + Sr(NO_3)_2 + 4H_2O \rightarrow 3Mg(OH)_2 + Sr(NO_2)_2 + H_2$. DSC studies have confirmed that the formation of strontium nitrite during ageing has a significant influence on the high temperature pyrotechnic reaction between magnesium and strontium nitrate.

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

1. Introduction

Thermal techniques are powerful methods for the characterisation of pyrotechnic compositions. These are typically based on mixtures of finely divided metal powders with inorganic oxidising agents [1]. The compositions have a wide range of applications utilising the production of light, heat, sound or smoke [2]. A high light output is required for compositions that are used as flares or tracers and in these cases magnesium powder is frequently employed as the fuel.

Pyrotechnic compositions containing magnesium can degrade during storage. As discussed previously [3], the technique of isothermal heat flow calorimetry is sufficiently sensitive to study the ageing process directly in the temperature range from 25 to 70 °C. We have reported the application of microcalorimetry to examine the ageing of a 50% magnesium–50% strontium nitrate composition in air at 50 °C and 65% relative humidity (RH) using closed ampoules [4]. Comparison of the results with those obtained for magnesium powder under the same conditions showed that, following an initial induction period, the pyrotechnic composition reacted at a much faster rate than the magnesium alone. This demonstrated that the ageing process, in the presence of water vapour, involved a direct reaction between strontium nitrate and magnesium.

The main reaction products of ageing were found to be magnesium hydroxide and strontium nitrite and the amounts

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* Corresponding author.
E-mail address: e.l.charsley@hud.ac.uk (E.L. Charsley).

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doi:10.1016/j.tca.2004.07.011

formed were correlated with the cumulative heats of ageing [4]. DSC studies showed that the formation of strontium nitrite had a significant influence on the high temperature pyrotechnic reaction between magnesium and strontium nitrate which resulted in a reduction in the ignition temperature of the composition. This increase in reactivity was in contrast to the expected behaviour where ageing normally reduces the reactivity of a pyrotechnic system and hence increases the ignition temperature.

The magnesium–strontium nitrate system does not seem to have been studied previously by isothermal microcalorimetry. Barišin et al. [5–8] 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 removed at intervals for examination by IR spectroscopy and X-ray diffraction. The results in our studies cannot be compared directly with those obtained by Barišin et al. This is due to the markedly higher humidities used in their work, which in some cases would have been above the deliquescence point of strontium nitrate [4].

In the present paper, the influence of the fuel to oxidant ratio on the extent and nature of the ageing process has been evaluated by studying magnesium–strontium nitrate compositions containing from 10 to 90% magnesium. The experiments have been carried out in air at 50 °C and 69% RH in closed ampoules. The RH has been increased from the value of 65% used previously to reduce the complications due to the variation in the time before the onset of the main reaction, which was observed at the lower humidity.

2. Experimental

The binary compositions were prepared from Grade 4 cut magnesium (to Defence Standard 13-130/1) and strontium nitrate (to Defence Standard 68-40/2). The strontium nitrate was dried at 80 °C and passed through a 125 μm sieve before use. Compositions containing from 10 to 90% magnesium in 10% increments were prepared by blending the components in a Turbula mixer.

Microcalorimetric measurements were performed on 100 mg samples at 50 °C and 69% RH using a Thermometric Model 2277 Thermal Activity Monitor. The samples were sealed into 3 cm^3 glass ampoules and the humidity was maintained using a saturated solution of sodium nitrate contained in a small tube placed in the ampoule. The experiments were carried out over a period of 28 days and the heat flow from the samples was monitored continuously throughout the ageing period.

The experimental procedures for analysis of the aged samples have been described previously [4]. The aged compositions were analysed for water and magnesium hydroxide content by thermogravimetry (TG), for nitrite using a spectrophotometric method and for nitrate using an ion selective electrode (ISE). Since nitrite interfered with the ISE measurements it was removed by the addition of sulphamic acid.

High temperature DSC under ignition conditions was carried out using an apparatus especially modified for pyrotechnic studies [9]. 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, over the temperature range ambient to 500 °C using a Mettler DSC 822^e. The measurements were made on 10 mg samples, in alumina crucibles with lids, at a heating rate of 10 °C min^{-1} in an argon atmosphere.

3. Results and discussion

3.1. Microcalorimetry studies

Preliminary experiments at 50 °C and 69% RH on the composition containing 50% magnesium confirmed the large reduction in induction period before the onset of the main reaction on increasing the relative humidity from 65 to 69% [4]. Duplicate experiments over a 28 day period gave good reproducibility and one of the curves is shown in Fig. 1. It can be seen that following an induction period of approximately 2 days, the heat flow signal rose rapidly to give a peak after 4 days. The heat flow decreased to a minimum after about 12 days and then increased slowly for the remainder of the experiment.

Selected heat flow curves for other compositions in the range are also given in Fig. 1. Apart from the sample containing 10% magnesium, all the compositions showed a well defined peak. The values obtained for the maximum heat flow signal increased with increasing magnesium content up to

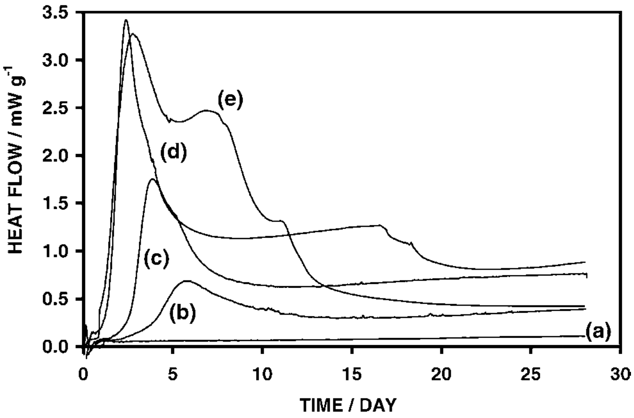

Fig. 1. Heat flow curves for magnesium–strontium nitrate compositions containing (a) 10% Mg, (b) 30% Mg, (c) 50% Mg, (d) 70% Mg and (e) 90% Mg (sample mass, 100 mg; 50 °C, 69% RH; atmosphere, air).

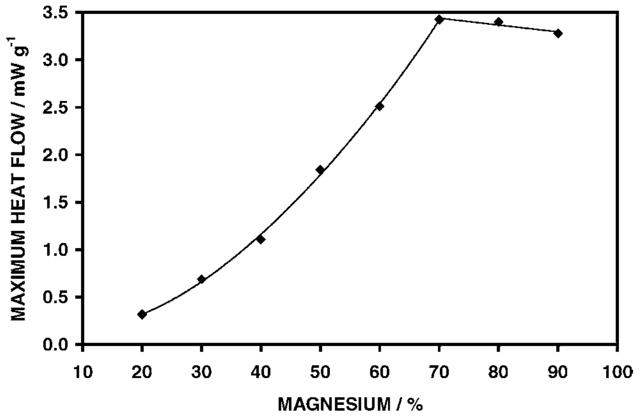

Fig. 2. Maximum heat flow signals for a range of magnesium–strontium nitrate compositions (sample mass, 100 mg; 50 °C, 69% RH; atmosphere, air).

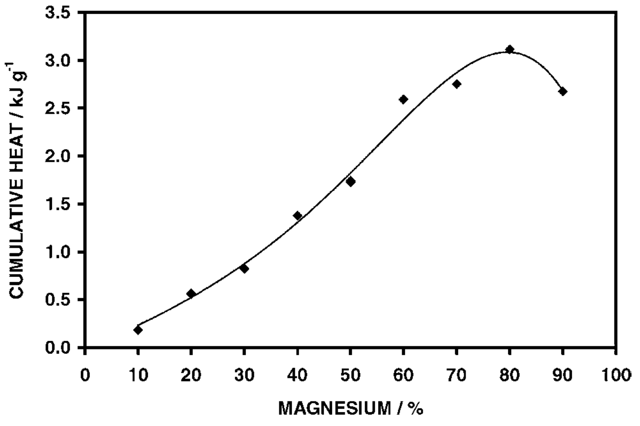

Fig. 3. Plot of cumulative heat at 28 days against magnesium content for a range of magnesium–strontium nitrate compositions (sample mass, 100 mg; 50 °C, 69% RH; atmosphere, air).

70% magnesium and then showed a small decrease (Fig. 2). A short induction period was observed before the onset of the main reaction and the time to reach the peak maximum decreased from over 6 days for the 20% magnesium composition to between 2 and 3 days for the compositions containing 70–90% magnesium.

The shape of the heat flow curves for the compositions containing 20–40% magnesium was similar to that observed for the 50% magnesium composition. However, for compositions containing more than 50% magnesium the curves showed a discrete reduction or step change in the signal following the peak maximum. The time to the onset of the step change showed a linear decrease with increasing magnesium content and reduced from about 22 days for the 60% magnesium composition to below 8 days for the sample containing 90% magnesium. The magnitude of the step increased from 20 μW g^{-1} at the 60% magnesium level to 2050 μW g^{-1} for the 90% magnesium composition and occurred in two stages for the compositions containing from 70 to 90% magnesium. These changes are discussed later in the context of the analytical results.

The cumulative heat measured over 28 days for the individual compositions is plotted as a function of magnesium content in Fig. 3. The total amount of heat evolved increased with the magnesium content up to 80% magnesium and showed a small decrease for the 90% magnesium composition. In addition, there appeared to be a correlation between the maximum heat flow signal and the total cumulative heat for each composition.

Microcalorimetry measurements on the 50% magnesium composition in an argon atmosphere gave similar results to those obtained in air, as did a single experiment on the 70% magnesium composition. The presence of oxygen does not therefore seem to be playing a significant part in the reaction between magnesium and strontium nitrate up to 70% magnesium. At higher magnesium levels there was some indication of increased reaction in the presence of air but further work would be required to confirm this.

The results of the magnesium hydroxide determinations on the aged compositions are shown in Fig. 4, together with the measured water contents. The amount of hydroxide present increased with magnesium content and reached a maximum of 29.5% at 70% magnesium. The water content increased linearly with increasing magnesium concentration and reached a maximum value of 2% at 60% magnesium. At higher magnesium concentrations the amount of water present decreased.

The amount of strontium nitrate in the aged composition decreased in a linear manner with increasing magnesium content and at 60% magnesium only about 3% of nitrate remained (Fig. 5). Strontium nitrite was present in all the aged compositions with the exception of the composition containing 90% magnesium. The amount of nitrite increased with increasing magnesium content and reached a maximum value of 18.7% for the composition containing 60% magnesium (Fig. 5). The nitrite present then decreased rapidly on increasing the magnesium content further and only 1% nitrite was found in the

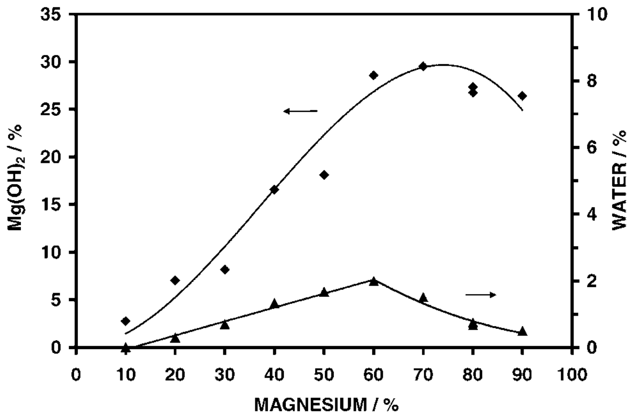

Fig. 4. Plot of magnesium hydroxide and water contents for a range of magnesium–strontium nitrate compositions aged at 50 °C, 69% RH in air for 28 days.

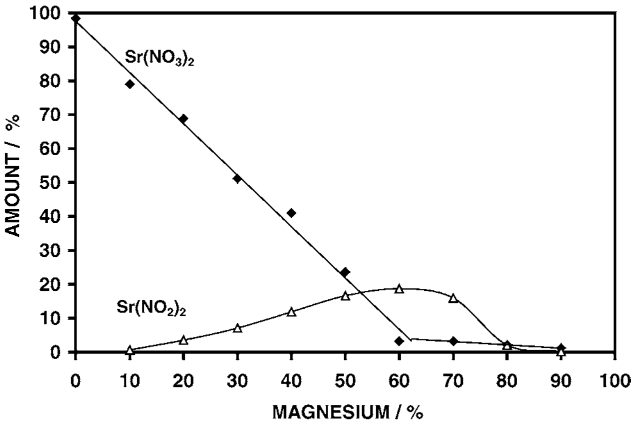

Fig. 5. Plot of strontium nitrate and nitrite content against magnesium content for a range of magnesium–strontium nitrate compositions aged at 50 °C, 69% RH in air for 28 days.

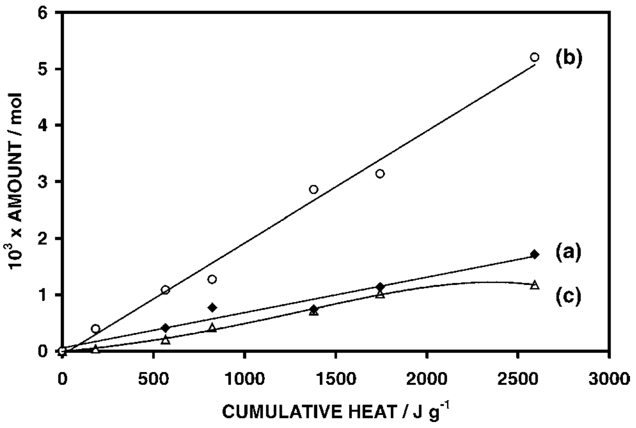

Fig. 6. Plot of (a) strontium nitrate reacted, (b) magnesium hydroxide formed and (c) strontium nitrite formed against cumulative heat for a range of magnesium–strontium nitrate compositions aged at 50 °C, 69% RH in air for 28 days.

aged 80% magnesium composition. The amount of water in the aged compositions showed a direct correlation with the amount of nitrite formed indicating that the nitrite was converted into the monohydrate.

The analytical results for strontium nitrate and nitrite lead to a possible explanation for the steps observed in the heat flow curves for compositions containing 60% and above of magnesium. In these compositions there is only a small amount of nitrate remaining at the end of the ageing process. Strontium nitrite was found to be absent in the aged residue from the composition containing 90% magnesium and there was only 1% present in the residue from the 80% magnesium composition. The rapid decrease in the heat flow is therefore considered to be related to the exhaustion of the nitrate and for the compositions containing 80 and 90% magnesium also nitrite.

The amount of magnesium hydroxide present in the aged composition was corrected for the increase in mass of the sample on ageing to give the amount present in 1 g of composition. The amount formed was then obtained by subtracting the hydroxide values determined for the unaged compositions. A similar approach was used to determine the amount of strontium nitrate reacted and the amount of strontium nitrite formed.

The results are plotted as a function of cumulative heat for compositions containing up to 60% magnesium in Fig. 6. It can be seen that the consumption of strontium nitrate and the production of magnesium hydroxide are both linear functions of cumulative heat. The ratio of the slopes indicate that approximately 3 mol of magnesium hydroxide are formed for each mol of strontium nitrate reacted. This indicates that a major component of the ageing process of the magnesium–strontium nitrate system may be represented by Eq. (1).

$$3Mg + Sr(NO_3)_2 + 4H_2O \rightarrow 3Mg(OH)_2 + Sr(NO_2)_2 + H_2 \qquad (1)$$

The cumulative heat for a sample mass of 1 g is plotted as a function of the amount of magnesium reacted in Fig. 7. The values for magnesium were calculated from the amount of magnesium hydroxide formed on the assumption that no other magnesium products were formed. The slope of this plot gave an internal energy of reaction of $-20.5\,kJ\,g^{-1}$ of magnesium. The standard thermodynamic internal energy change calculated from Eq. 1, assuming that the water is in the gas phase, is $-21.7\,kJ\,g^{-1}$ of magnesium (the standard state values relate to 25 °C, but the heat capacity correction to 50 °C will be small). The closeness of these results lends support to the proposed reaction stoichiometry. However, it should be noted that contribution to the overall heat of reaction from the hydration of the anhydrous strontium nitrite has been neglected, since a value for the heat of formation of the monohydrate does not appear to be available.

It can be seen from Fig. 5 that the amount of strontium nitrite present decreased rapidly as the magnesium

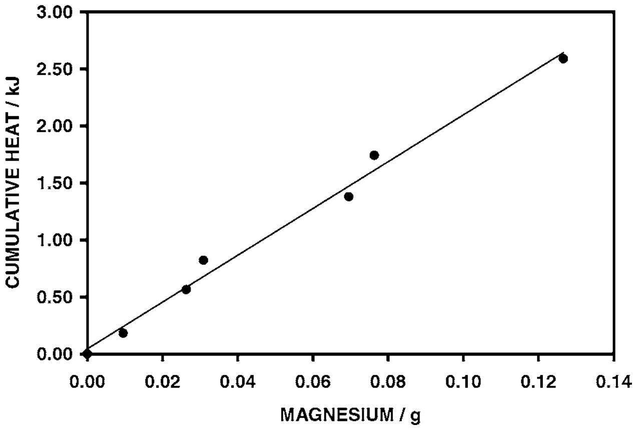

Fig. 7. Plot of cumulative heat for a sample mass of 1 g against amount of magnesium reacted for a range of magnesium–strontium nitrate compositions aged at 50 °C, 69% RH in air for 28 days.

concentration was increased above 70%. This indicates that strontium nitrite can react with magnesium in the presence of moisture. Since strontium nitrite is not available commercially, a sample is being synthesised and microcalorimetry studies will be performed on a magnesium–strontium nitrite mixture to ascertain the nature and extent of the reaction.

3.2. DSC studies

DSC has been used to evaluated the influence of ageing on the reactivity of the compositions by comparing the results obtained for aged and unaged compositions. The experiments were carried out under both ignition and non-ignition conditions.

Studies on the unaged compositions under ignition conditions showed that ignition was achieved for samples containing from 20 to 80% magnesium. Representative curves are shown in Fig. 8, together with a plot for strontium nitrate obtained under the same conditions. For the compositions containing 40 to 80% magnesium, a single exothermic peak was given which resulted in ignition. A more complex pattern was observed for the lower magnesium content mixtures. This is considered to reflect the overlap of the exothermic pyrotechnic reaction with the fusion and decomposition of strontium nitrate, which was observed above 650 °C. The ignition temperatures are plotted as a function of magnesium content in Fig. 9 and show a reduction from about 640 °C for the 20% magnesium composition to 595 °C for the 40% magnesium composition. There were no marked changes in the ignition temperature on increasing the magnesium concentration further.

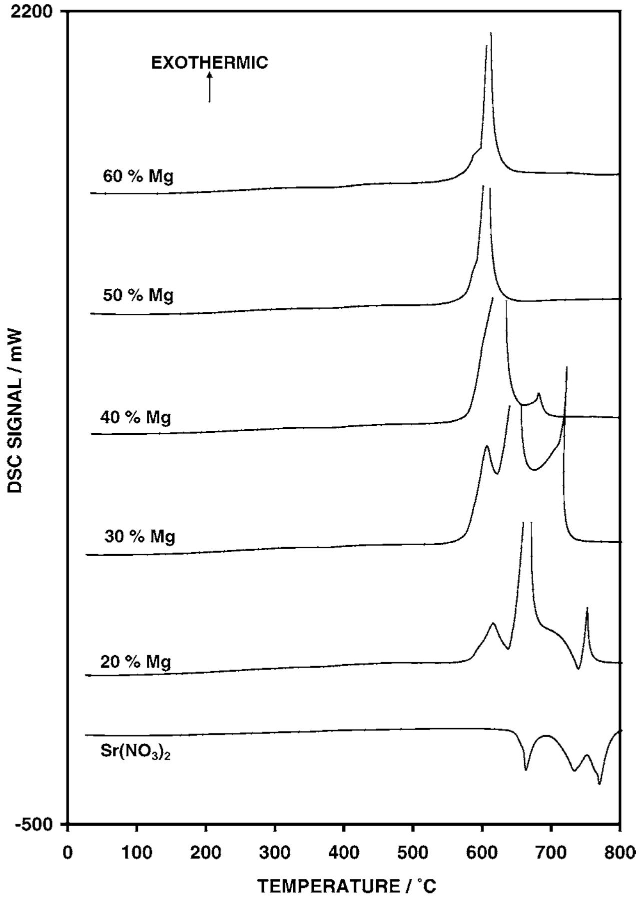

Fig. 8. DSC Curves under ignition conditions for a range of magnesium–strontium nitrate compositions (sample mass, 20 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

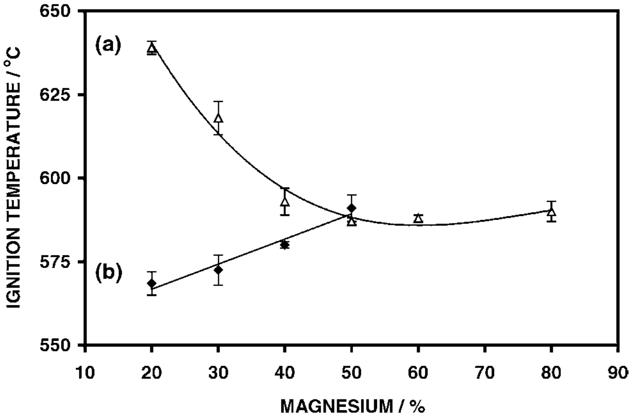

Fig. 9. Plot of ignition temperature against magnesium content for a range of magnesium–strontium nitrate compositions (a) unaged and (b) aged for 28 days in a closed ampoule in air at 50 °C and 69% RH (sample mass, 20 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

DSC measurements, under ignition conditions, on the aged compositions confirmed that the ageing process has a marked influence on the high temperature pyrotechnic reaction and ignition was only achieved for the compositions containing from 20 to 50% magnesium. Representative DSC curves are given in Fig. 10 and the ignition temperatures are plotted in Fig. 9. The aged compositions showed a linear increase in the ignition temperature with magnesium content rising from 570 °C for the 20% magnesium composition to 590 °C for the 50% magnesium composition. Comparison of the ignition temperatures for the aged and unaged compositions showed that the samples containing 20–40% magnesium gave a reduction in the ignition temperature on ageing. This was greatest for the composition containing 20% magnesium, which showed a decrease of some 70 °C. The reduction in the ignition temperature for a given composition on ageing decreased with increasing magnesium content and similar values were given for the 50% magnesium composition for both aged and unaged samples.

In our previous paper [4] we showed that at 50 °C and 65% RH the ignition temperature of the 50% Mg–50% $Sr(NO_3)_2$ composition decreased with increasing cumulative heat. A minimum value of 560 °C in the region of 700 J g^{-1} was given and the ignition temperature did not change significantly on further ageing to 1000 J g^{-1}. Studies in progress on this composition, where samples are being aged for different times at 50 °C and an increased humidity of 69% RH, show that similar ignition temperatures are obtained in the cumulative heat range 500–900 J g^{-1}. As the samples were aged to

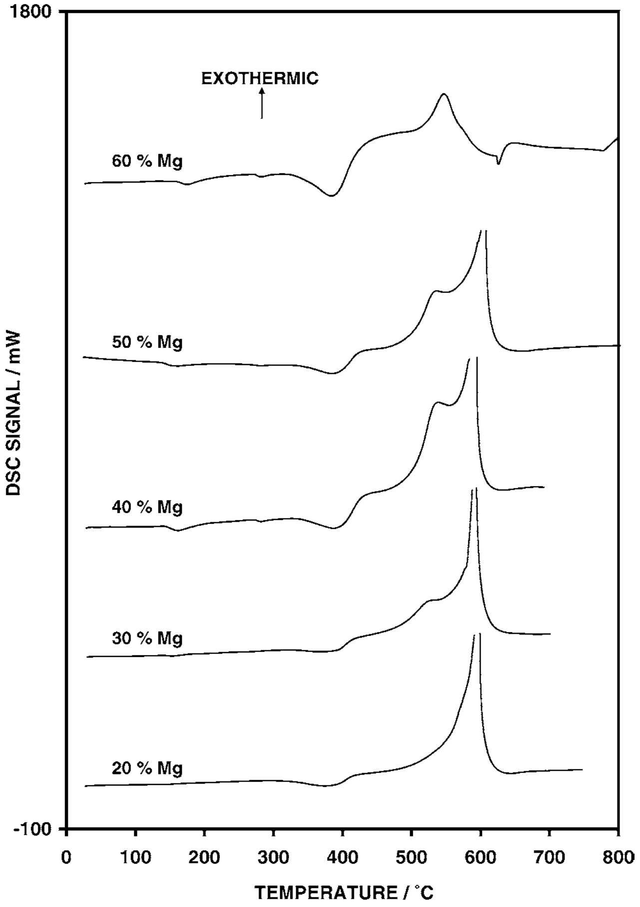

Fig. 10. DSC curves under ignition conditions for a range of magnesium–strontium nitrate compositions aged for 28 days in a closed ampoule in air at 50 °C and 69% RH (sample mass, 20 mg; heating rate, 50 °C min^{-1}; atmosphere, argon).

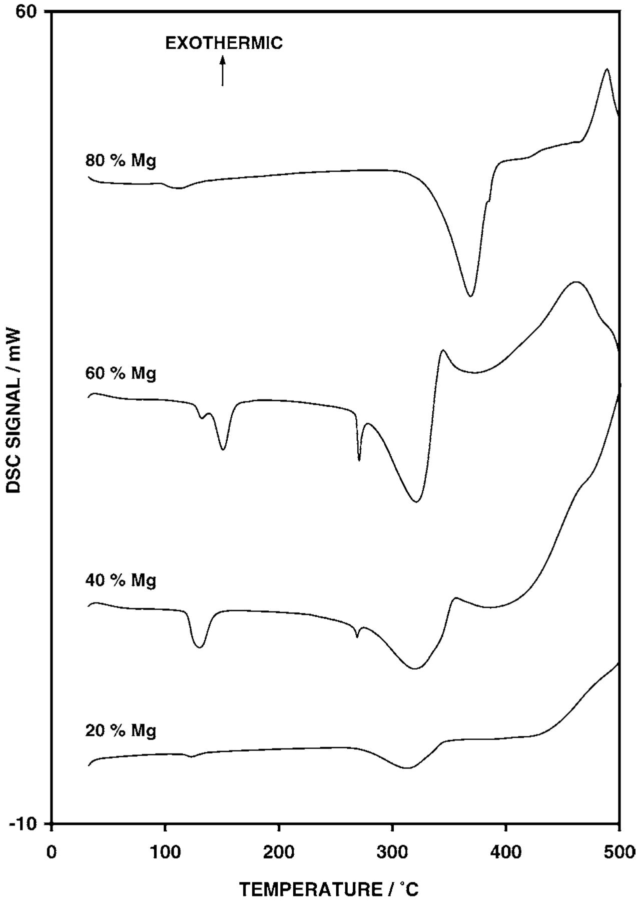

Fig. 11. Comparison of DSC curves for a range of magnesium–strontium nitrate compositions aged for 28 days in a closed ampoule in air at 50 °C and 69% RH (sample mass, 10 mg; heating rate, 10 °C min^{-1}; atmosphere, argon).

higher cumulative heats, the ignition temperature increased and as indicated above after 28 days (1700 J g^{-1}), were showing similar ignition temperatures to the unaged material.

It can be seen from a comparison of Figs. 8 and 10 that there are marked differences in the pre-ignition region between the unaged and aged compositions. In the unaged compositions there were no significant reactions below 550 °C. In contrast, the aged compositions all show exothermic reactions commencing above the endothermic peak due to the decomposition of magnesium hydroxide in the region of 400 °C. The initial part of these reactions is shown in more detail in the DSC curves in Fig. 11, which were obtained under non-ignition conditions.

We have attributed this exothermic reaction to the presence of strontium nitrite formed in the ageing process [4]. Strontium nitrite has been reported to melt and to undergo slow decomposition at about 360 °C [10]. This is supported by our recent work, using simultaneous TG-mass spectrometry, where we have observed that aged 50% magnesium–50% strontium nitrate samples evolved small amounts of NO above 260 °C and that the rate accelerated markedly above 400 °C [4]. Since strontium nitrate was found by TG-mass spectrometry to decompose above 570 °C [4], we considered that the nitrite could exhibit increased reactivity towards magnesium compared with the nitrate. The presence of nitrite was confirmed by the small endothermic peak at 270 °C on the DSC curves for compositions containing from 30 to 70% magnesium and is illustrated in Fig. 11 for the compositions containing 40 and 60% magnesium. The peak corresponds to the reported solid-solid transition in strontium nitrite [10].

The absence of significant low temperature exothermic reactions in the compositions containing more than 70% magnesium can be explained on the basis of the chemical analysis results. These show that significant amounts of strontium nitrite were not present.

4. Conclusions

Microcalorimetry studies on a range of magnesium–strontium nitrate compositions, in conjunction with chemical and thermal analysis measurements on the products of ageing, have enabled the influence of the fuel to oxidant ratio on the ageing process to be evaluated. The major products of ageing were found to be magnesium hydroxide and strontium nitrite. For aged compositions containing from 10 to 60% magnesium the consumption of strontium nitrate and the production of magnesium hydroxide were found to be linear functions of cumulative heat. The ratio of the slopes indicate that approximately 3 mol of magnesium hydroxide were formed for each mol of strontium nitrate reacted. This suggested that a major component of the ageing process of the magnesium–strontium nitrate system could be represented by the equation $3Mg + Sr(NO_3)_2 + 4H_2O \rightarrow 3Mg(OH)_2 + Sr(NO_2)_2 + H_2$ and that the mechanism of reaction was independent of the amount of fuel present. This has the important consequence that studies on a selected composition can be considered to be representative of the system as a whole. The absence of a significant effect

DSC studies have confirmed that the formation of strontium nitrite during the ageing process has a significant influence on the high temperature pyrotechnic reaction between magnesium and strontium nitrate. Compositions containing from 20 to 40% magnesium gave a reduction in the ignition temperature on ageing for 28 days. This was largest for the composition containing 20% magnesium, which showed a decrease of some 70 °C This increase in reactivity is in contrast to the expected behaviour where ageing normally reduces the reactivity of a pyrotechnic system.

In the present study all of the measurements have been carried out on compositions aged to a fixed time. In order to confirm the reaction stoichiometry proposed above, experiments are now in progress to follow the reaction of magnesium with strontium nitrate as a function of time, using a 50% Mg–50% $Sr(NO_3)_2$ composition. It is intended to age the samples sufficiently to react all the nitrate present. This should enable the contribution of the magnesium–strontium nitrite reaction to the overall heat flow signal to be assessed. In addition, ageing studies will be carried out on magnesium–strontium nitrite mixtures prepared using a sample of strontium nitrite, which is currently being synthesised.

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