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# An investigation of strontium nitrite and its role in the ageing of the magnesium–strontium nitrate pyrotechnic system using isothermal microcalorimetry and thermal analysis techniques

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## Abstract

A sample of strontium nitrite has been synthesised and thermally characterised to investigate its role in the ageing of magnesium–strontium nitrate pyrotechnic compositions in the presence of water vapour. Studies by isothermal microcalorimetry show that the addition of strontium nitrite to a 50% magnesium–50% strontium nitrate composition eliminated the induction reaction normally observed in closed ampoule studies in air at 50 °C and relative humidities in the range 65–69%.

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

## 1. Introduction

Pyrotechnic formulations containing magnesium and strontium nitrate are used for signalling, area illumination and as tracers for ammunition [1]. The degradation of these compositions during storage can result in reduced performance and ultimately in failure to function.

In previous work, we have investigated the ageing of this pyrotechnic system using isothermal microcalorimetry in conjunction with thermal and chemical analyses [2–4]. We have also reported the pyrotechnic properties for a range of compositions containing 10–90% magnesium [5]. The ageing studies were carried out in air at 50 °C over a range of relative humidity (RH) values using closed ampoules. The heat flow curves at 65% RH for a 50% magnesium–50% strontium nitrate composition showed an extended induction period before the onset of the main degradation reaction [2]. The latter reaction resulted in the formation of magnesium hydroxide and strontium nitrite. Increasing the RH to 69% reduced the time of the induction period and at RH values of 74% and above an induction period was not observed [3].

Experiments were also performed on a range of compositions containing 10–90% magnesium at 50 °C and 69% RH for a period of 28 days [4]. Quantitative analysis of the aged material for magnesium hydroxide and strontium nitrite showed that a major component of the ageing process could 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 analysis results suggested that the strontium nitrite formed during this reaction also reacted with magnesium since the measured amount of nitrite decreased in aged compositions containing high levels of magnesium.

To clarify the role of strontium nitrite in the ageing of the magnesium–strontium nitrate system, a sample of strontium nitrite monohydrate has been synthesised. Previous thermal analysis studies have shown that the anhydrous nitrite undergoes

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a solid–solid transition from an orthorhombic to a cubic structure. The reported temperatures for this transition ranged from 265 °C to 274 °C [6–8]. Determination of the fusion temperature of the salt is complicated by the fact that some decomposition takes place in this region [7]. Values for the temperature of fusion ranged from 362 °C to 395 °C [6–9]. Bureau [10] obtained a much lower value of 276 °C, using a heating curve method, which is close to the values given for the solid–solid transition.

In view of the variation in the above temperatures and the limited number of studies carried out on this material, strontium nitrite monohydrate was characterised by a number of thermal methods, prior to studying its influence on the magnesium–strontium nitrate system. The latter studies were performed by isothermal microcalorimetry and DSC. These techniques have been used to investigate both the reaction of strontium nitrite with magnesium and the influence of the nitrite on the reaction between magnesium and strontium nitrate. No previous studies appear to have been carried out on magnesium-based compositions containing strontium nitrite.

## 2. Experimental

### 2.1. Preparation of strontium nitrite

Silver nitrite dissolved in a minimum quantity of 0.88 g $cm^{-3}$ ammonia solution was added drop-wise, with stirring, to a cold (approximately 10 °C) saturated solution of strontium chloride hexahydrate. As the silver chloride precipitated from solution the stirring rate was increased and more water was added. The resulting suspension was boiled under a stream of nitrogen for approximately 1–2 h to remove the ammonia. The silver chloride precipitate was hot filtered, washed with hot water and discarded. The water was removed from the filtrate by heating at 70–80 °C under vacuum in a rotary evaporator. The white crystals of strontium nitrite monohydrate obtained were recrystallised from a minimum amount of ethanol. The strontium nitrite was analysed for nitrite content by the spectrophotometric method described previously [2]. The water content was determined by thermogravimetry.

### 2.2. Preparation of compositions

Binary compositions containing equal parts by mass of Grade 4 cut magnesium (to Defence Standard 13-130/1) and either strontium nitrate (to Defence Standard 68-40/2) or strontium nitrite monohydrate were prepared by sieve mixing. Ternary magnesium–strontium nitrate–strontium nitrite compositions were made by sieve mixing the appropriate amount of strontium nitrite monohydrate with a 50% magnesium–50% strontium nitrate composition.

### 2.3. Strontium nitrite characterisation

Preliminary DSC studies on the strontium nitrite monohydrate were performed using a Mettler DSC $822^e$ fitted with a robotic sample changer and IntraCooler. The 5 mg samples were heated at 10 °C $min^{-1}$ in encapsulated aluminium crucibles, with a pinhole in the lid. The experiments were performed in an argon atmosphere over the range −50 °C to 400 °C.

The temperature of the solid–solid transition was determined by heating 10 mg samples in encapsulated aluminium crucibles at 3 °C $min^{-1}$ in an argon atmosphere. The crucibles were sealed after the water of crystallisation had been removed by a preliminary heating to 200 °C. Similar conditions were used to measure the fusion temperature, but the heating rate was increased to 10 °C $min^{-1}$ to minimise the amount of decomposition. The instrument was calibrated using the melting points of tin and lead (at 3 °C $min^{-1}$) for the solid–solid transition and lead and zinc (at 10 °C $min^{-1}$) for the fusion. The temperature of fusion was also determined with a TA Instruments DSC 2920 under the same experimental conditions.

Simultaneous TG–mass spectrometry (MS) was performed with a Du Pont TG 951 thermobalance linked via a heated capillary to a VG Quadrupoles GasLab 300 mass spectrometer. The 10 mg samples were heated at 10 °C $min^{-1}$ in alumina crucibles in an argon atmosphere.

Sample controlled thermogravimetry (SCTG) studies were performed on 10 mg samples in an argon atmosphere, with a modified Stanton Redcroft TG-1000 thermobalance [11].

The equilibrium relative humidity of strontium nitrite monohydrate was determined using a Thermometric Model 2277 Thermal Activity Monitor fitted with a Relative Humidity Perfusion (RHP) cell. The measurements were performed at 50 °C, in air flowing at 100 $cm^3\,h^{-1}$, on an 80 mg sample of strontium nitrite to which 50 μl of water had been added to form a paste. The equilibrium RH was determined from the zero heat flow signal obtained by plotting the measured heat flow signal against the applied RH. The RHP cell was calibrated initially with a saturated solution of potassium chloride which has a mean equilibrium relative humidity of $81.2 \pm 0.2\%$ at 50 °C [12].

### 2.4. Magnesium–strontium nitrite/nitrate compositions

Isothermal microcalorimetry experiments, with the Thermometric Model 2277 Thermal Activity Monitor, were performed in air at 50 °C on 100 mg samples in 3 $cm^3$ closed glass ampoules. A small tube containing a saturated solution of potassium iodide or sodium nitrate was placed inside the ampoule to maintain the RH at either 65% or 69%, respectively.

DSC measurements were made with a chromel plate high temperature DSC apparatus [13]. For these experiments, 10 mg samples were heated in quartz crucibles at 10 °C $min^{-1}$ in an argon atmosphere.

## 3. Results and discussion

### 3.1. Strontium nitrite

The determined water and nitrite contents for the synthesised strontium nitrite monohydrate are 9.1% and 46.2%, respectively. These are in good agreement with the theoretical values of 9.1% and 46.6%.

DSC studies at 10 °C $min^{-1}$ showed three endothermic peaks corresponding to the loss of water of crystallisation, the

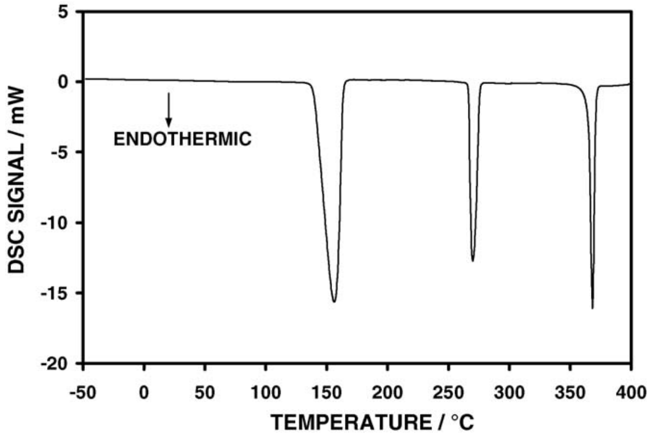

Fig. 1. DSC curve for $Sr(NO_2)_2{\cdot}H_2O$ (sample mass, 5 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

solid–solid phase transition and the fusion of the salt (Fig. 1). The measured value for the extrapolated onset temperatures ($T_e$) for the solid–solid transition was 265.7 ± 0.1 °C and is between the values of 265 °C and 267 °C measured by Liminga et al. [8] and Warrington et al. [7], respectively. The values measured for the fusion temperature using two different DSC systems were in good agreement and a mean value of 362.7 ± 0.4 °C was obtained. This value is also intermediate between those of Warrington et al. [7], 362 °C, and Liminga et al. [8], 364 °C.

The thermal stability of the strontium nitrite monohydrate was investigated by simultaneous TG–MS over the range 25–500 °C. The TG curve and evolved gas profiles are shown in Fig. 2. Following the rapid evolution of the water of crystallisation, the decomposition of the nitrite was observed to commence at 350 °C with the evolution of NO. This is in reasonable agreement with the work of Warrington et al. [7] who obtained a value of 360 °C for 1% decomposition, when a sample was heated at 5 °C $min^{-1}$ in a helium atmosphere. Experiments performed to higher temperatures showed that the other main decomposition product $O_2$ was not observed until the sample temperature was above 600 °C. The overall mass loss compared well with the theoretical loss of 47.6% for the dehydration of the nitrite and decomposition to form strontium oxide.

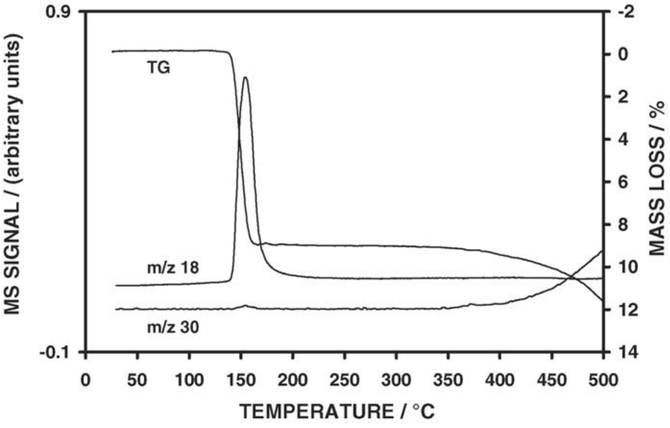

Fig. 2. TG–MS curves for $Sr(NO_2)_2{\cdot}H_2O$ (sample mass, 10 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

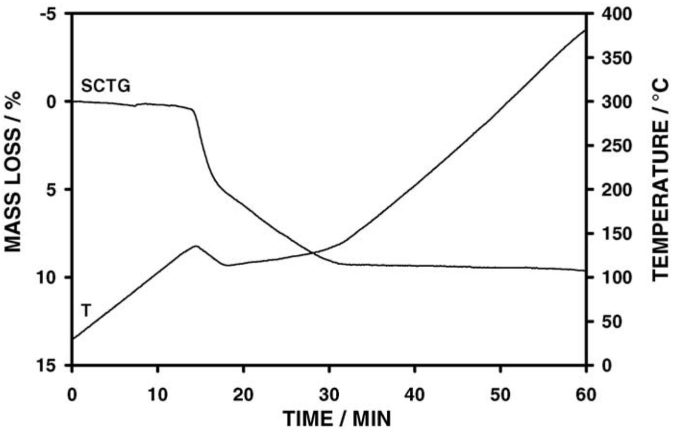

Fig. 3. SCTG curves for $Sr(NO_2)_2{\cdot}H_2O$ (sample mass, 10 mg; heating rate, ±10 °C $min^{-1}$; atmosphere, argon).

The rapid water loss observed during the TG–MS experiments was investigated further by sample controlled thermogravimetry. The mass loss and temperature curves, given in Fig. 3, show that as soon as onset of mass loss occurred in the region of 135 °C the sample was cooled. The sample temperature had to be reduced to around 110 °C before the pre-set rate of mass loss was achieved. The sample was then heated slowly for the remainder of the mass loss which was completed at 135 °C. This type of behaviour is typical of a mechanism involving nucleation and growth of nuclei [14] and explains the rapid rate of reaction under linear heating conditions.

It was of particular relevance to the ageing studies to determine the relative equilibrium humidity of $Sr(NO_2)_2{\cdot}H_2O$. This was measured using the technique described above as 79.2% and may be compared with the value of 82.4% determined for $Sr(NO_3)_2$ [3]. These results indicate that the microcalorimetry studies on the pyrotechnic compositions are being carried out at RH levels well below the deliquescence points of both oxidising agents.

### *3.2. Microcalorimetry studies on magnesium–strontium nitrite and magnesium–strontium nitrate–strontium nitrite compositions*

Microcalorimetry experiments performed on a 50% Mg–50% $Sr(NO_2)_2{\cdot}H_2O$ composition at 50 °C and 65% RH showed an initial induction period of 3 days (Fig. 4). The reaction accelerated after 7 days and began to slow after 10 days reaching a plateau at about 24 days. An increase in the heat flow over the next 7 days was then observed. Similar features were observed on increasing the humidity to 69%. However, as shown in Fig. 4, the events took place at shorter times and higher heat flow signals were given. These results show that strontium nitrite can react with magnesium under conditions of elevated temperature and humidity. This explains the decrease in the amount of nitrite found in Mg–$Sr(NO_3)_2$ compositions containing 60% or more magnesium, when they were aged for 28 days at 50 °C and 69% RH [4].

Comparison of the curves for the 50% Mg–50% $Sr(NO_2)_2{\cdot}H_2O$ and 50% Mg–50% $Sr(NO_3)_2$ compositions

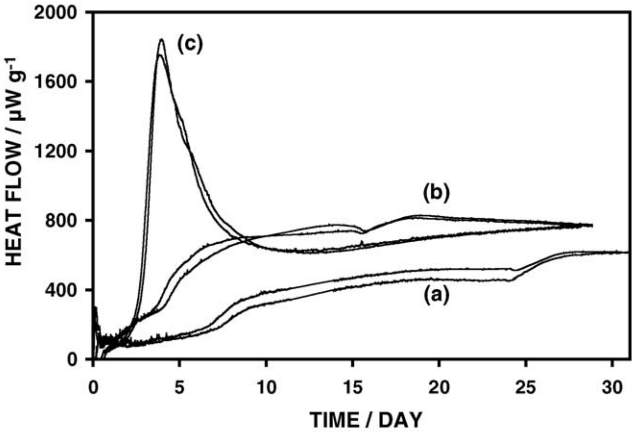

Fig. 4. Heat flow curves for a 50% Mg–50% $Sr(NO_2)_2{\cdot}H_2O$ composition at (a) 65% RH and (b) 69% RH and (c) for a 50% Mg–50% $Sr(NO_3)_2$ composition at 69% RH (sample mass, 100 mg; temperature, 50 °C; atmosphere, air).

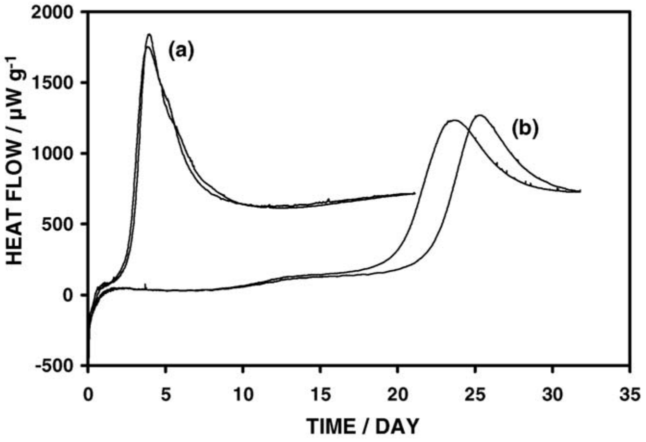

Fig. 6. Heat flow curves for a 50% Mg–50% $Sr(NO_3)_2$ composition (a) unaged and (b) aged for 30 months under ambient storage conditions (sample mass, 100 mg; temperature, 50 °C; 69% RH; atmosphere, air).

obtained at 50 °C and 69% RH showed that both gave an initial induction period of about 2 days (Fig. 4). However, a much higher reaction rate was observed for the nitrate composition which reached a peak maximum of about 1800 $\mu W\,g^{-1}$ at 3.9 days. The heat flow signals for the nitrate composition then decreased rapidly and after approximately 8.5 days were lower than those for the nitrite composition. After 28 days had elapsed, similar heat flow signals were observed for both compositions.

The influence of strontium nitrite on the ageing of a magnesium–strontium nitrate composition is shown in Fig. 5, where duplicate heat flow curves obtained at 50 °C and 69% RH for a 50% Mg–50% $Sr(NO_3)_2$ composition and the same composition with the addition of 11% $Sr(NO_2)_2{\cdot}H_2O$ are compared. The introduction of strontium nitrite into the nitrate composition eliminated the induction period and in one experiment the heat flow signal exceeded the set instrument range (300 µW) after only 0.1 days. The heat flow signals decayed more rapidly than those for the binary compositions and after 12 days similar values were given. Since the magnesium–strontium nitrite composition showed an induction period, it would appear that the presence of both the nitrate and nitrite is required to remove the induction period.

The ageing taking place when a 50% Mg–50% $Sr(NO_3)_2$ composition was stored under ambient conditions was found to have a marked influence on the induction period. This is illustrated in Fig. 6 where the heat flow curves obtained for the composition at times approximately 30 months apart are compared. The induction period has increased on storage from the original value of about 2 days to between 20 and 22 days. The stored composition was found to contain an increased amount of magnesium hydroxide but strontium nitrite was absent.

The long induction period shown by the stored composition has allowed the effectiveness of strontium nitrite at reducing the induction reaction to be studied. Ternary compositions containing 0.1%, 1% and 11% strontium nitrite monohydrate were examined by microcalorimetry at 50 °C and 69% RH. Representative heat flow curves for the compositions containing 1% and 11% strontium nitrite monohydrate are compared with those obtained for the aged binary composition in Fig. 7 and it can

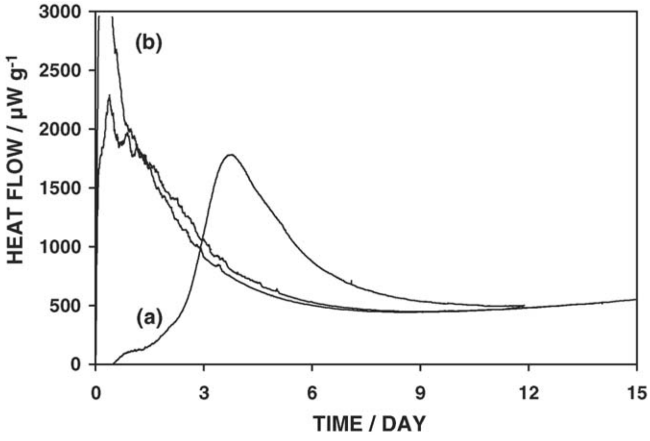

Fig. 5. Heat flow curves for compositions containing (a) 50% Mg–50% $Sr(NO_3)_2$ and (b) 44.5% Mg–44.5% $Sr(NO_3)_2$–11% $Sr(NO_2)_2{\cdot}H_2O$ (sample mass, 100 mg; temperature, 50 °C; 69% RH; atmosphere, air).

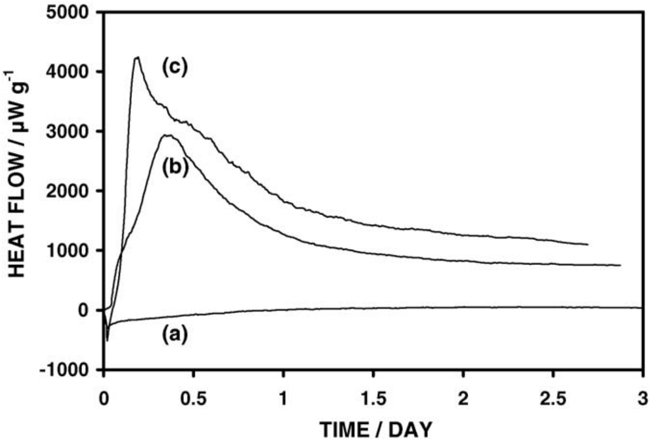

Fig. 7. Heat flow curves for compositions containing (a) 50% Mg–50% $Sr(NO_3)_2$ with (b) 1% $Sr(NO_2)_2{\cdot}H_2O$ and (c) 11% $Sr(NO_2)_2{\cdot}H_2O$ added (sample mass, 100 mg; temperature, 50 °C; 69% RH; atmosphere, air).

be seen that the addition of as little as 1% strontium nitrite monohydrate has eliminated the observed induction reaction. In the case of the mixture containing 0.1% nitrite although the induction reaction was not eliminated, the time to reach the maximum heat flow signal was significantly reduced (12.8 ± 0.7 days in comparison with 24.5 ± 0.5 days for the binary composition).

### *3.3. DSC studies on the incorporation of strontium nitrite into the magnesium–strontium nitrate system*

A feature of the DSC curves for the aged Mg–$Sr(NO_3)_2$ compositions has been the presence of a pre-ignition exothermic reaction above 300 °C, which overlapped with the endothermic peak resulting from the decomposition of magnesium hydroxide formed in the ageing process [2,4]. This is illustrated in Fig. 8 where a DSC curve for a 50% Mg–50% $Sr(NO_3)_2$ composition, aged at 50 °C and 69% RH, is compared with a curve obtained for the unaged composition, which did not show any exothermic reaction in the range 100–500 °C.

The presence of a pre-ignition reaction and its enhancement with increasing extent of ageing was attributed to the presence of strontium nitrite formed in the ageing process [2,4]. However, it can be seen from the DSC curve for the 50% Mg–50% $Sr(NO_2)_2{\cdot}H_2O$ mixture in Fig. 9 that only a small amount of low temperature exothermic activity was observed.

In contrast, it can also be seen from Fig. 9 that the addition of 11% of strontium nitrite monohydrate to the 50% magnesium–50% strontium nitrate composition has markedly increased the magnitude of the low temperature exothermic reaction compared with that for the magnesium–strontium nitrite reaction. The results clearly show that the additional exothermicity observed in DSC experiments on aged compositions is due to the influence of strontium nitrite on the magnesium–strontium nitrate reaction rather than to the direct reaction between magnesium and strontium nitrite.

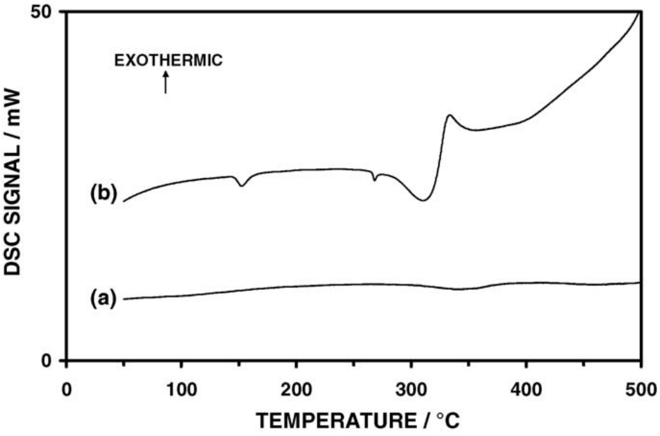

Fig. 8. DSC curves for a 50% Mg–50% $Sr(NO_3)_2$ composition (a) unaged and (b) aged in air at 50 °C and 65% RH to a cumulative heat of 1013 J $g^{-1}$ (sample mass, 10 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

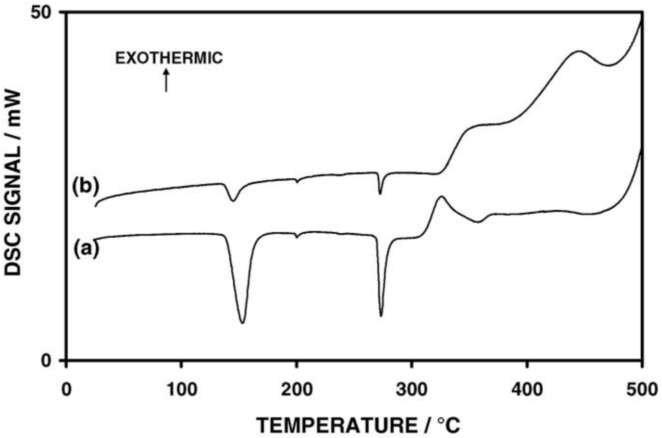

Fig. 9. DSC curves for compositions containing (a) 50% Mg–50% $Sr(NO_2)_2{\cdot}H_2O$ and (b) 44.5% Mg–44.5% $Sr(NO_3)_2$–11% $Sr(NO_2)_2{\cdot}H_2O$ (sample mass, 10 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

The possibility of the exothermic reaction being initiated by eutectic formation between strontium nitrite and strontium nitrate was investigated by carrying out DSC measurements on a mixture containing equal parts by mass of the two salts. No clear eutectic melt was observed although a shallow endothermic peak was given at 374 °C in place of the well defined fusion peak of the nitrite. This peak started at about 320 °C, which is in the region of the onset temperature of the initial exothermic reaction. Thermomicroscopy on the mixture showed the onset of partial fusion above 330 °C; however, solid material was still present at 400 °C. It therefore appears that the presence of strontium nitrate lowers the melting point of the nitrite, hence initiating the exothermic reaction.

## 4. Conclusions

A sample of strontium nitrite monohydrate has been synthesised. Dehydration in the region of 130 °C was shown by sample controlled thermal analysis to take place by a nucleation and growth mechanism. Temperatures for solid–solid phase transition and fusion were measured in sealed crucibles as 265.7 ± 0.1 °C and 362.7 ± 0.4 °C, respectively. A small amount of decomposition was found to take place in an open crucible above 350 °C with the evolution of NO. The equilibrium relative humidity of the strontium nitrite monohydrate at 50 °C was determined as 79.2% compared with a value of 82.4% obtained for strontium nitrate.

Isothermal microcalorimetry studies have shown that strontium nitrite can react with magnesium at 50 °C and RH values of 65% or 69%. However, the rate of reaction appeared to be slower than that between strontium nitrate and magnesium. The addition of as little as 1% strontium nitrite monohydrate was found to eliminate the induction reaction observed in the Mg–$Sr(NO_3)_2$ system and its role is therefore considered to be autocatalytic. DSC studies have shown that the increased exothermic activity in aged magnesium–strontium nitrate compositions is due to influence of strontium nitrite on magnesium–strontium nitrate reaction, rather than to direct reaction of the nitrite with magnesium.

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