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A NEW TYPE OF HIGH PRESSURE SYSTEM FOR A TIAN-CALVET CALORIMETER

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Abstract

A Tian-Calvet heat flux calorimeter has been modified for use with high pressures in measurements of thermal hazards of materials. The system comprising a specially designed high pressure vessel and an associated manifold is described. With this system, comparative measurements using both standard and high pressure vessels can be made, different materials and/or liners can be used for the high pressure vessel and an assessment of the influence of the gaseous environment on thermal behaviour can be made. Calibration was carried out in the range 25 to 300°C at different pressures and heating rates, using sapphire and the calibration results were verified with benzoic acid, both reference grade materials. With the new vessel, pressures up to about 70 MPa can be used or recorded during the thermal decomposition of energetic materials.

The reproducibility of the baseline, as illustrated by standard error results, was about 0.02% compared with 0.13% for the standard vessel, over the entire temperature range. The corresponding results for the baseline of the pressure vessel at 5.5 MPa (in air and Ar) and in a calibration experiment with sapphire were 0.08%.

Experimental data obtained for ammonium nitrate and 2,3-dimethyl-2,3-dinitrobutane in the standard and pressure vessels are compared and discussed. The effect of pressure and the nature of the gaseous environment (inert or oxidizing) on the results for these two materials will be described.

Keywords: AN, DMNB, heat flux calorimeter, high pressure system

Introduction

Heat flux calorimetry has been used in many research areas, including the study of the thermal hazard of energetic materials. As a result of the nature of the reactions of energetic materials, the reaction vessels are required to be able to withstand dynamic pressures up to about 50 MPa. The upper pressure limit of

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some commercial pressure vessels is about 10 MPa [1] and it is believed that these vessels have only been tested under static condition. Thus this type of vessel is generally not suitable for high pressure studies using energetic materials. This paper will describe a new type of high pressure system for a heat flux calorimeter (HFC). The system includes a specially designed high pressure vessel, a manifold, a pressure transducer and a data acquisition system. Also, results obtained for ammonium nitrate (AN) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) in the HFC will be presented and discussed.

Experimental

A matched pair of high pressure vessels was made from 17-4PH stainless steel. The vessels were designed and fabricated at the National Research Council of Canada (NRCC); each vessel was rated to 70 MPa and had an internal volume of about 5 cm^3. A schematic of the vessel assembly is shown in Fig. 1. The seal between the vessel and the transfer tube was made with a metal gasket, and that

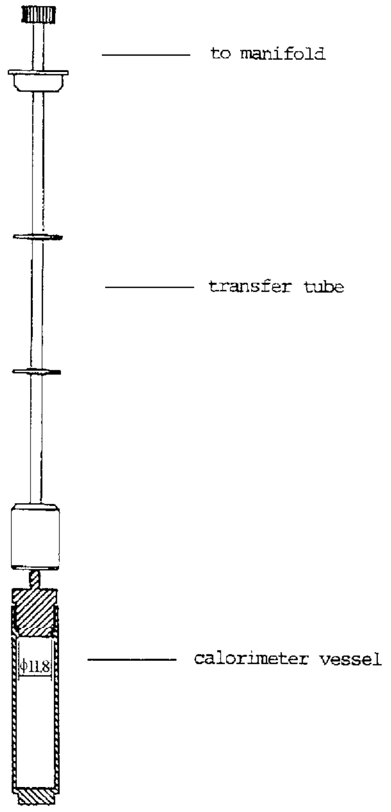

Fig. 1 Schematic of the experimental vessel

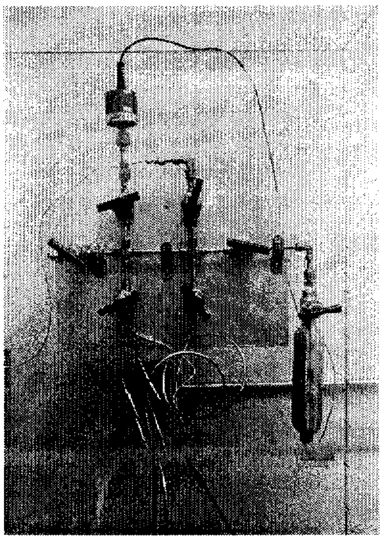

Fig. 2 Photograph of the manifold

between the transfer tube and the manifold was made with a viton O-ring. The manifold, also fabricated at NRCC, is shown in Fig. 2; the valves and stainless steel tubing used were also rated to 70 MPa. The volume of the manifold is about 12 cm^3. Experiments have not, as yet, been undertaken at 70 MPa since a suitable remote device for operating the valves is still being developed. The transmitter (Setra, Model C206) used had a pressure range of 34 or 68 MPa, with a full scale accuracy of 0.14%.

The HFC used was a Setaram C 80, twin cell Tian-Calvet instrument. It has a massive aluminum block with two identical cylindrical cavities for sample and reference cells located symmetrically about the centre. For safety reasons a special protective cage of 1.3 cm Lexan was built around the HFC. A sliding panel in front permitted loading the vessels, and the top of the cage was open. The assembly including HFC is shown in Fig. 3.

Sapphire (α-Al_2O_3) and benzoic acid obtained from the NRCC with a National Bureau of Standards Certificate [2–4] were used, respectively for calibration and verification. Ammonium nitrate (AN) supplied by Baker was used without further treatment and 2,3-dimethyl-2,3-dinitrobutane (DMNB) of 98 mol% purity was supplied by the Aldrich Company. Sample sizes of about 200 mg AN and 50 mg of DMNB were used in the HFC studies, compared with about 1 mg of AN and DMNB used in the DSC measurements. All of the DSC studies were done using glass microampoules as the sample container [5]. Heating rates of 0.3 and 1°C min^{-1} were used in the HFC measurements. Data acquisition and control functions for the calorimeter were performed using the software supplied by

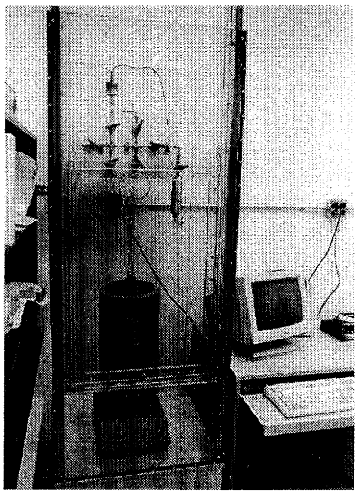

Fig. 3 Photograph of HFC with the cage

Setaram. Pressure readings were collected by interfacing the transmitter to a separate computer via a data shuttle express from Strawberry Tree. The two software packages collected readings at synchronized time intervals.

Results and discussion

Figure 4 shows the reproducibility of the baseline for the high pressure vessels. The standard error of these results is about 0.02%. The baselines for the

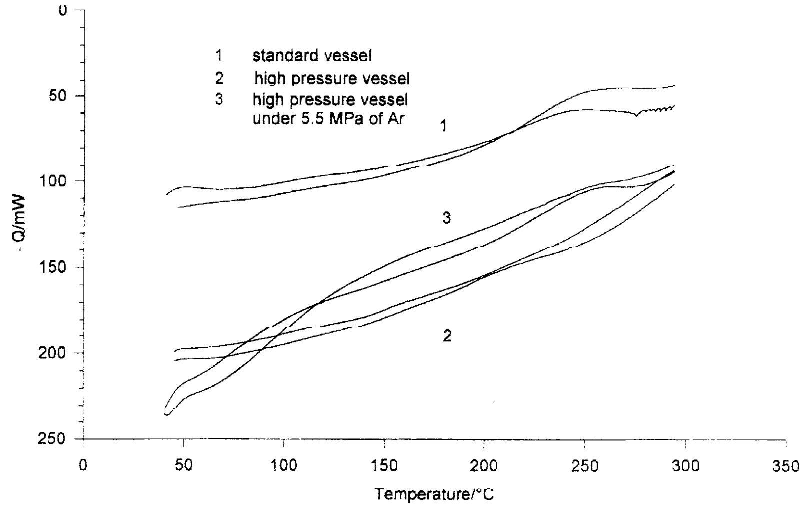

Fig. 4 Reproducibility of baseline curves

standard vessels are also shown in Fig. 4. The standard error of the baseline for the standard vessel is about 0.13%. Baseline experiments were also carried out in 5.5 MPa of argon. These results are also shown in Fig. 4. The standard error is 0.08%. Reference grade sapphire was used for testing the sensitivity of the high pressure vessels in the HFC [6]. The reproducibility of the experiments was 0.08%. The results are shown in Fig. 5. After baseline and sensitivity calibration, reference grade benzoic acid was used to verify calibration. The literature value

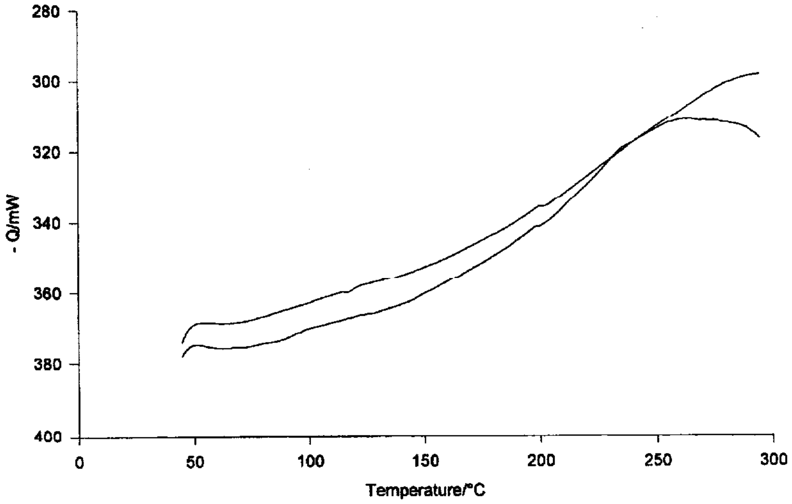

Fig. 5 Reproducibility of signal calibration using sapphire

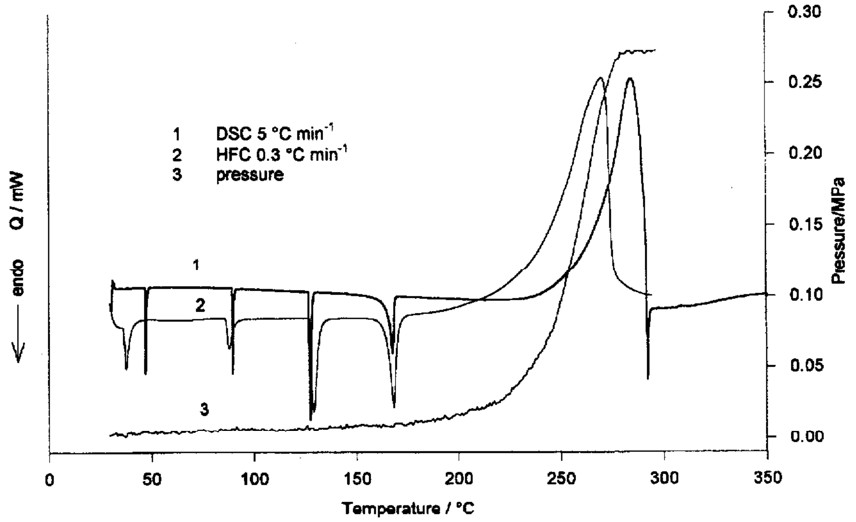

Fig. 6 Thermal study of ammonium nitrate by DSC and HFC

[7] for benzoic acid is ΔH=141 J g^{-1} and T_{melt}=122.45°C. Our experimental results were ΔH=143±1 J g^{-1} and T_{melt}=123.3±0.7°C.

Table 1 Thermochemical data for ammonium nitrate

Phase	[1]DSC	[2]ΔH/J g^{-1}	HFC	[3]T/°C
IV–III	17.6±0.7	17.05	16.9±0.6	42.3
III–II	17.9±0.6	17.42	17.6±0.4	86.6
II–I	54.8±1.1	55.16	57.9±0.7	127.3
Fusion	82.4±1.4	75.98	77.6±1.2	169.8

[1] Ref. [12], [2] Ref. [13, 14, 7] [3] From Fig. 6

The results for AN obtained from the HFC and DSC are compared in Fig. 6. The enthalpy changes for the phase transitions obtained from DSC and HFC are compared in Table 1. From Table 1 it is found that the enthalpy change for each solid phase transition obtained from both DSC and HFC are in agreement, only the heats of fusion are different, but the heat of fusion determined by HFC is in better agreement with literature values, even though, as seen in Fig. 6, the final baseline for this transition could not be established as the HFC reached its upper temperature limit. It is likely that melting and evaporation of AN occur simultaneously in the HFC because of the larger free volume (including the reaction vessels and the manifold) available. That the melting or evaporation transition in HFC followed smoothly is indicated by the steep and smooth rise in pressure during the thermal event. In the DSC a glass microampoule was used as a sample

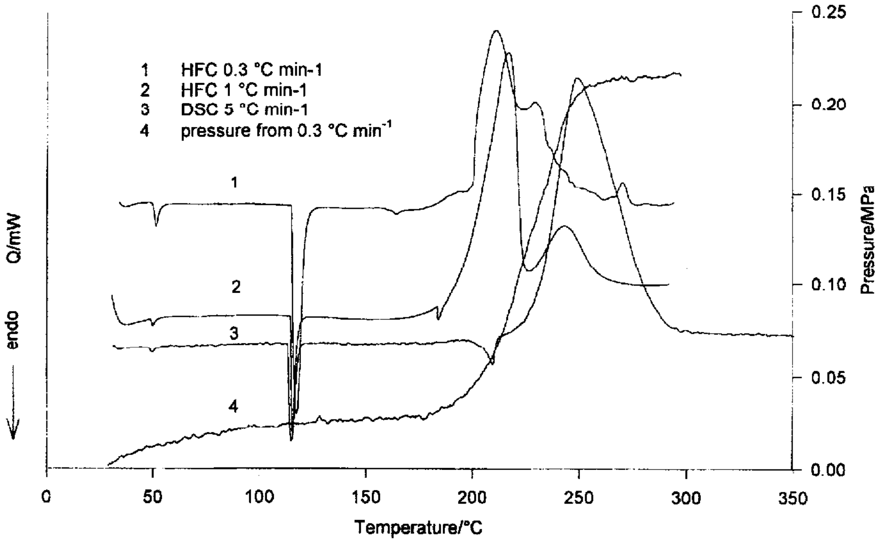

Fig. 7 Thermal study of DMNB using DSC and HFC

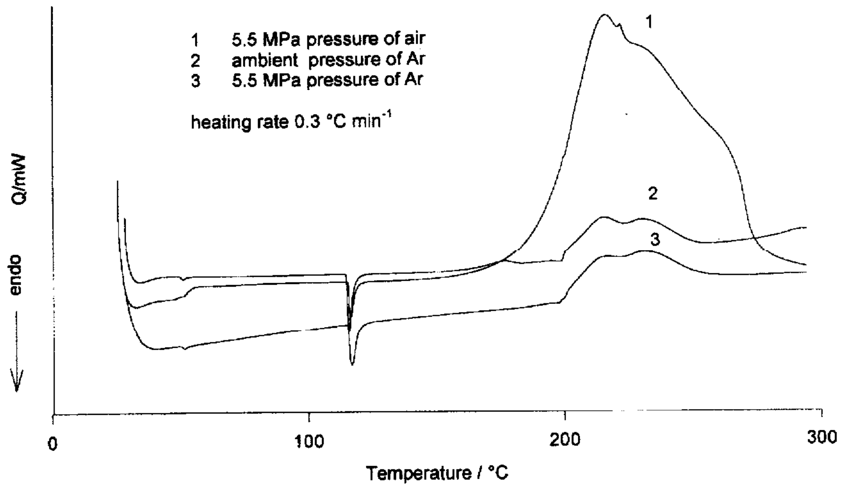

Fig. 8 Thermal study of DMNB under different pressures in HFC

Table 2 Thermochemical data for DMNB

Phase	ΔH/J g^{-1}		T*/°C
	DSC	HFC	
I–II	5.7±1.1	5.4±0.4	49.8
II–III	103±9	102±4	114.6
Exotherm	–3080±270	–2520±360	199.5

* From Fig. 7

container. The microampoule has a relative free volume of significantly lesser amount than the HFC system, so very little evaporation took place.

The thermal properties for DMNB have been studied using the DSC and accelerating rate calorimeter (ARC) in our laboratory previously [8–10]. Recently, a HFC was used to study the thermal properties of DMNB [11]. Three experimental conditions were used in the HFC, ambient pressure of argon and 5.5 MPa of both argon and air. The results are shown in Figs 7 and 8. In all cases complex exothermic reactions were observed. The heat of the reaction at ambient and high pressure of argon are similar, but the heat of reaction under high pressure of air is much larger than that under high pressure of argon. The results are listed in Table 2. It is also seen from Table 2 that the ΔH obtained from HFC is smaller than that obtained from DSC. The difference can be attributed to the volatility of DMNB, so that sublimation actually takes place at temperatures above the II→III phase transition. Because the HFC system has a larger free volume some of the DMNB sublimes prior to the chemical reaction. This leads to a large difference in the heat capacity before and after the reaction. Consequently, the uncertainty in the ΔH derived from the HFC experiments is larger than that obtained from the DSC results.

Conclusions

Heat flux calorimetry is an effective method to study thermal hazard of energetic materials, especially, with high pressure vessels and manifold. It has been shown that the high pressure vessel performs satisfactorily in comparison with the standard vessel in the HFC. Because larger samples are used the experimental results are closer to real conditions, particularly for mixtures of samples. The results obtained for AN are generally in agreement with the results obtained by DSC measurements and also with those reported in the literature. In the presence of high pressure of air early oxidation of DMNB took place and an exothermic reaction with a large ΔH occurred, which was not seen in the DSC experiments.

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