Specific Heat of HMX

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Abstract

THE specific heat of octahydro-1,3,5, 7-tetranitro-1,3,5,7 tetrazocine (HMX) was determined by the use of a differential scanning calorimeter (DSC). The specific heat for both crystalline and powered samples was obtained from 294 to 445 K for the beta phase and from 410 to 485 K for the delta phase. The specific heat results were fitted to least squares polynomials to allow the interpolation of the data between points and extrapolation with appropriate care to higher temperatures. The effects of partially decomposed HMX samples on the specific heat were investigated also.

Contents

A Perkin-Elmer DSC-2 Differential Scanning Calorimeter was used for the specific heat determinations. A Perkin-Elmer flow-through cover was installed to decrease the amount of contamination to the enclosure due to decomposition and vaporization of the sample. Nitrogen gas was allowed to pass continuously through the enclosure and cover, thus purging out most of the evolving gases from the sample.

The DSC measures the differential power required to keep a sample's temperature rising at a given rate when compared to that of a standard reference material. The specific heat of the sample is then calculated from the following equation:

$$C_{p_{\mathrm{sam}}} = C_{p_{\mathrm{std}}} \frac{M_{\mathrm{std}}}{M_{\mathrm{sam}}} \left[\frac{(\mathrm{d}q/\mathrm{d}t)_{\mathrm{sam}}}{(\mathrm{d}q/\mathrm{d}t)_{\mathrm{std}}} \right]$$

where M_{std} is the mass of the standard reference material, M_{sam} the mass of the sample, $C_{p_{\mathrm{std}}}$ the specific heat of the sample, and $(\mathrm{d}q/\mathrm{d}t)_{\mathrm{sam}}/(\mathrm{d}q/\mathrm{d}t)_{\mathrm{std}}$ the differential power output from the DSC. All of the specific heat measurements were made using a sapphire standard obtained from the National Bureau of Standards (NBS). The data collection and analysis were done using a digital computer system.

The crystalline samples were prepared by cleaving a large crystal of HMX until a single crystal small enough to fit into the DSC sample pan was obtained. The crystal samples were typically 5 mm square × 1 mm thick and weighed about 17 mg. The highly pure, large crystals were grown and furnished by Boggs et al.[1] The electrochemical analysis of the crystals showed the concentration of the major impurity, RDX, to be less than 0.1%.

Powder samples consisted of a blend of various particle sizes and were 99.7% pure HMX. Sample masses of about 19 mg were used. Descriptions of the powders are given in Table 1.

Specific heat results for the beta phase are shown in Fig. 1 for the single crystal and the powdered blend HMX samples heated at a rate of 5 K/min. To assure that the samples were not being heated too rapidly during the specific heat measurements, resulting in erroneous specific heat values, several samples were measured at rates of 2.5 K/min and 10 K/min. The results were no different than those in the figure. The samples were measured over a temperature range of 294-445 K. The difference between the specific heat of the single crystal and powdered samples was at the experimental error limit of 3%. Figure 1 also contains the results of Velicky et al.[2] Krien et al.,[3] Rylance and Stubley,[4] and Wilcox.[5] Velicky et al. used an ice calorimeter, while the others used DSCs. The differences are at the 6% level.

The beta HMX was transformed to delta phase using the DSC, which allowed the observation of the transformation. Repeated runs with the DSC verified that the transformation was complete and that the delta phase did not immediately transform back to the beta phase. The transformation started near the temperatures reported in the literature.[2,6] The sample could not be cooled below 400 K without some of the HMX transforming back to the beta phase. The upper limit for the specific heat measurement for the delta phase was 486 K because of appreciable sample decomposition above that temperature. The delta phase results for both single crystal and powdered HMX are reported in Fig. 2 along with the data reported by Krien et al.[3] and Rylance and Stubley.[4] The specific heat values of the powdered HMX were again approximately 3% higher than the single crystal results. The specific heat for the beta and delta phases was fit to a least squares cubic polynomial. The least squares coefficients are tabulated in Table 2.

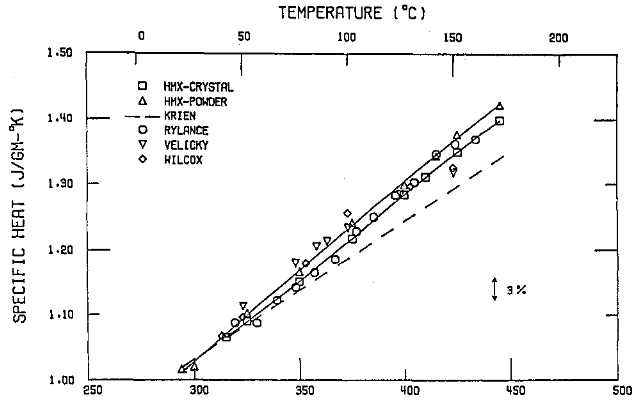

Fig. 1 Specific heat of beta HMX.

Table 1 Purity and blend information for HMX powdered samples

Material	Holston lot No.	Particle size, μm	Percent occupying blend	Percent HMX (purity)
HMX	5486	18.9	50	99.7
HMX	7016	6.0	30	99.7
HMX	7016	3.3	20	99.7

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Table 2 Least squares results

	a	b	c	d
Beta phase				
Single crystal	0.9802919	$0.1720238E-02$	$0.8463956E-05$	$-0.2505766E-07$
Powder	0.9701549	$0.2272406E-02$	$0.4814534E-05$	$-0.1555766E-07$
Delta phase				
Single crystal	$-0.3032355E+01$	$0.7193665E-01$	$-0.3929727E-03$	$0.7257188E-06$
Powder	$-0.1914304E+01$	$0.5269194E-01$	$-0.2841281E-03$	$0.5290091E-06$

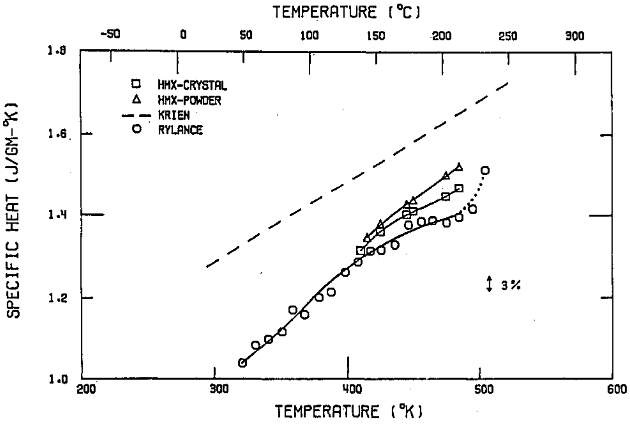

Fig. 2 Specific heat of delta HMX.

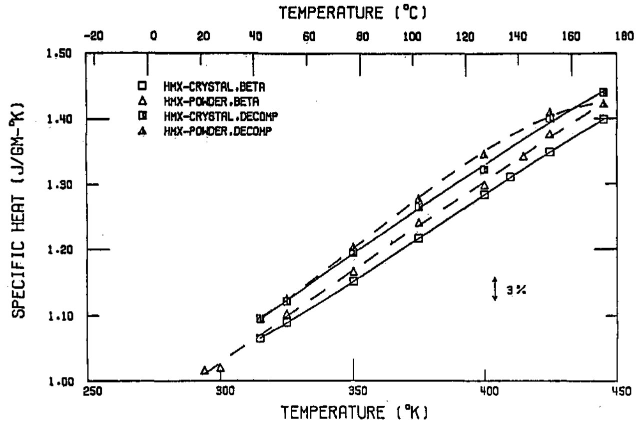

Fig. 3 Specific heat of partially decomposed HMX.

Samples that had undergone some decomposition were measured to determine how sensitive the specific heat is to decomposition. The samples were prepared by heating them in a furnace at 510 K until approximately one-eighth of their original mass had been lost. There was no attempt to determine the amount of decomposition products in the samples. The specific heat was then determined over the temperature range of 315-445 K which was below the temperature where significant decomposition occurred. The results are plotted in Fig. 3. Samples that had undergone no decomposition and partially decomposed samples are shown for comparison in the figure. The partially decomposed samples had a specific heat approximately 6% higher than the virgin samples for both the single crystal and powdered HMX. There was no beta to delta transformation observed during the specific heat measurement, which indicates that the HMX was in the delta phase. The samples were weighed before and after the DSC run to check for additional decomposition. However, the mass loss was insignificant. After leaving the samples set at room temperature for several days and remeasuring them, the beta to delta phase transformation was observed again.

Acknowledgments

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