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CHARACTERIZATION OF ENERGETIC MATERIAL RESPONSE TO THERMAL ENVIRONMENTS*

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ABSTRACT

Results of experiments designed to characterize the pressure-time response of heated, confined energetic materials are presented. These experiments were aimed at characterizing the state of energetic material near ignition, but were not intended to be cookoff tests. We examined several materials, including HMX, TATB, PBX 9501, PBX 9502 and Al/AP/HTPB propellant. We observed complex coupling between the mechanical and chemical response of these decomposing materials and could observe phase transitions, endo- and exothermic reactions and gas pressurization. Samples were recovered for postmortem examination of chemical and physical changes.

INTRODUCTION

Prediction of violence-of-reaction in cookoff of energetic materials (EMs) is being pursued by many groups. This is a complex issue with many material parameters contributing to potential outcomes. We focused some attention recently on characterizing the material in its thermally damaged state, or what it looks like just before ignition occurs. Time-to-event experiments do not address specifically the evolved gas pressure and properties such as cracking and porosity. Because the chemistry and mechanics are closely coupled the formation of gases via chemical decomposition can cause cracks and voids to form and some of these voids may later collapse under the increased load from the gas pressure. In a previous report we described a "hot cell" experiment aimed at uncovering some of these behaviors.[1] At that time we had modified our apparatus to minimize thermally induced stresses in the assembly. Our present results were obtained using that redesigned fixture. These were not intended to be "cookoff" experiments. They allowed us to monitor some of the behavior of the energetic material during heating, such as thermal expansion, phase transitions, gas pressurization and structural collapse. They also provide us with samples for postmortem examination to characterize microstructural and chemical changes. In this paper we present experimental results on several energetic materials. Another paper presented at this meeting deals with detailed analysis and modeling of our results, primarily related to HMX. [2]

EXPERIMENTAL

The Hot Cell experiment allows us to determine the chemical decomposition and mechanical response of a confined EM at elevated temperature, and is shown schematically in Fig. 1. Briefly, confined HE is subjected to an arbitrary thermal field (up to 260°C) and the HE surface temperature and the forces generated by material expansion and gas generation are measured. This experiment was designed to minimize free volume ensuring that reactive products remain in contact with the energetic material. Explosive pellets (typically 6.35 mm diameter by 3.17 mm thick), were pressed to the desired densities at either Mason & Hangar Pantex Plant or at Sandia National Laboratories. The pellets were sealed inside the cylindrical stainless steel cell by opposing Invar pistons with o-ring seals made of either silicone or Viton providing gas confinement up to several thousand psi. The bottom piston was threaded into a load cell and the top piston usually contained a thermocouple to measure the surface temperature of the energetic material.

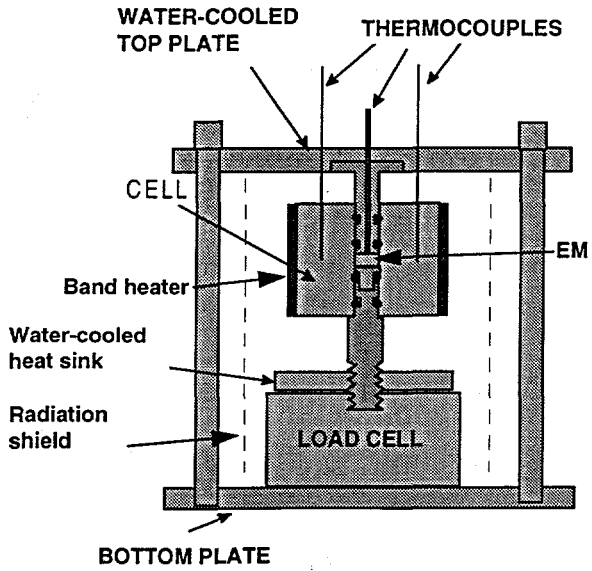

Fig. 1. Schematic of experimental assembly

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DISCLAIMER

Invar bolts were used to assemble the fixture to an adequate preload to assure proper mechanical response. Cooling and radiation shielding were provided to protect the load cell and to minimize thermally-induced stress relief in the bolts. The cell was heated with a band heater and cell temperatures were measured with thermocouples. The experiment was conducted inside a vacuum chamber with the valve to the pump nearly closed so that we could detect any significant leak from the cell without interference from slow outgassing from the heated assembly itself. After heating, samples were extracted for postmortem examination for both chemical decomposition and morphology changes.

RESULTS

Even though we tried to optimize this design to avoid thermally-induced relief in the fixture, it was not perfectly stiff. We performed several experiments on inert materials to make sure that the experiment was behaving in a repeatable and reliable fashion. Figure 2 shows a typical trace for an inert material, copper, heated in this assembly. We observed an increase in the measured load with temperature due to the thermal expansion of the copper. At final temperature the load remained unchanged. Unloading generally followed the same temperature-pressure curve as loading. The lowest temperature reading was always from the thermocouple in contact with the pellet surface due to the active cooling along the axis of the fixture. Energetic materials, of course, were expected to behave differently from inerts with reactive pressurization and phase changes anticipated. Figure 3 shows results obtained for PBX 9501 (95% HMX, 2.5% Estane, 2.5% BDNPA/F) at 1.84 g cm^{-3} density.

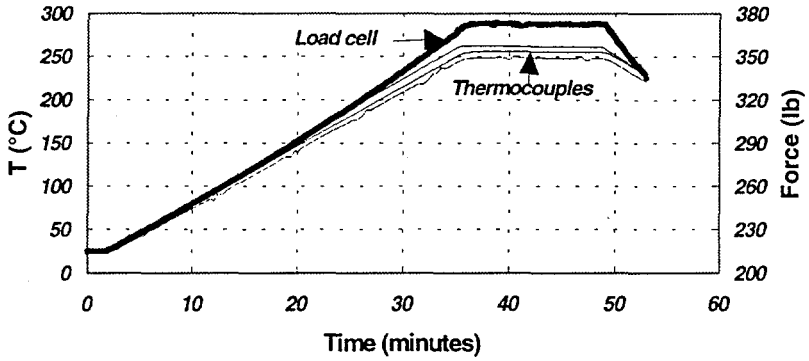

Fig. 2. Temperature and Force vs. Time data for copper heated in the hot cell assembly.

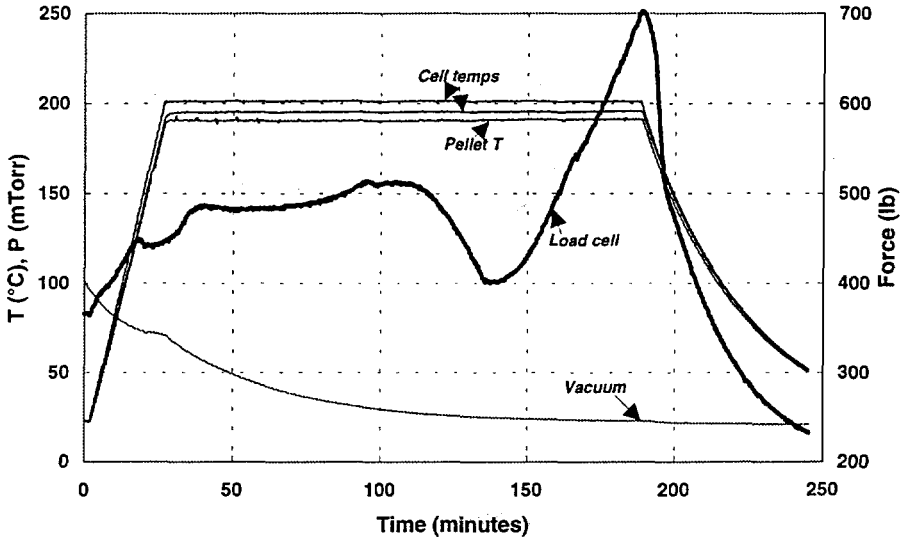

Fig. 3. Temperature, Force and vacuum pressure vs. Time data for PBX 9501 heated in the hot cell assembly.

The measured force indicated thermal expansion of the material during the heating process. Before the β-δ HMX phase transition temperature (near 170°C), the load decreased and was followed by another gradual increase until after final temperature was achieved. A large decrease in load, consistent with a reduction in volume of the confined material occurred later in time (near 130 minutes in Fig. 3), was followed by a more rapid increase in the force. This

experiment was halted by turning off the heater at a point where the data from the load cell was no longer in calibration and where we became concerned that the material might cookoff. Note that the vacuum signal never showed any abrupt increase, which we interpret to mean that the hot cell remained leak-free. Similar results were obtained in four separate experiments showing good reproducibility and some variation with temperature consistent with faster reactions at higher temperatures.

In reviewing these data on PBX 9501 we were surprised at the effect of the β-δ HMX phase transition[3] because we expected to observe a dramatic increase in load. After confirming that the experiment was in fact reproducible, we chose to examine pure HMX (Class A powder, 1.80 g cm^{-3} density) eliminating any possible effects due to binder behavior. Results are shown in Fig. 4 for two HMX runs at different temperatures. Only the pellet temperatures and the load cell force readings are displayed for these two runs.

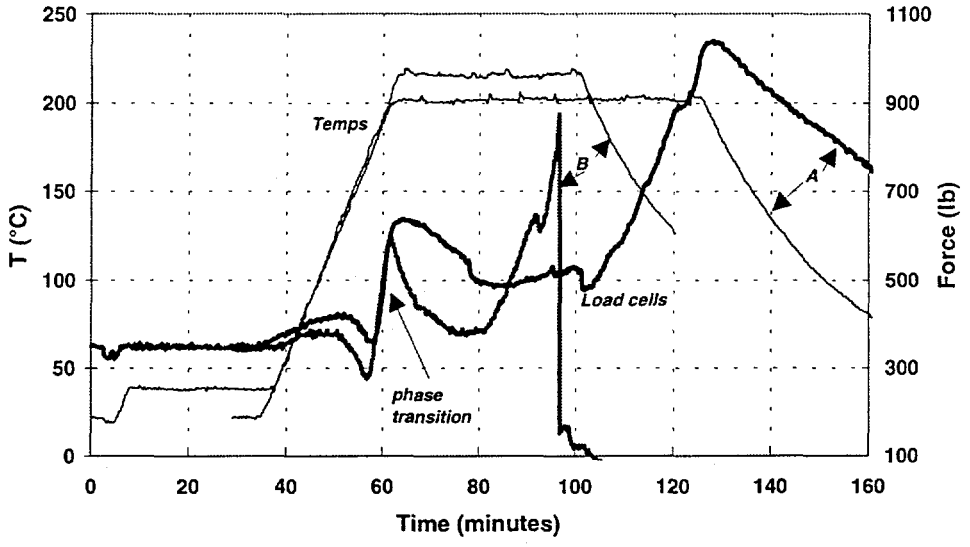

Fig. 4. Pellet temperature and Force vs. Time data for two separate runs (indicated A and B) with HMX heated in the hot cell assembly.

One set of data is displaced in time so that it overlaps the heating ramp of the other experiment. The lower temperature run was halted by turning off the heater at a point where the load cell would be out of calibration. The second experiment was ended when the hot cell vented. This vent was detected by the vacuum reading (not displayed). In these experiments we observed a more gradual expansion at low temperatures followed by a decrease in load, consistent with softening of the HMX crystals, just prior to the abrupt phase transition. After the phase transition, and at constant temperature, the measured load decreased and then increased due to reactions generating gas pressures. Clearly, processes occurred faster for the pellet heated to the higher temperature, and the features were in good agreement for all experiments performed.

Other materials studied included TATB, PBX 9502 (at two different densities) and an Al/AP/HTPB propellant. We were encouraged to note that results for each material were always reproducible. The reaction products from the propellant caused significant corrosion of the stainless steel cell and we are investigating alternate cell materials to minimize this effect.

Postmortem examination of the heated pellets included density, HPLC (high performance liquid chromatography), IC (ion chromatography), FTIR (Fourier transform infrared) and SEM (scanning electron microscopy). Most of these were cursory investigations to determine the utility of each technique in providing insight into reactive and physical mechanisms. Figure 5 shows SEM results for PBX 9501. Rather than unheated baseline material we chose to compare the decomposed PBX 9501 (hot cell data shown in Fig. 3) with a sample that had been heated through the

phase transition and then immediately cooled. Both pellets were cleaved and several SEM photographs were taken at various locations and magnifications.

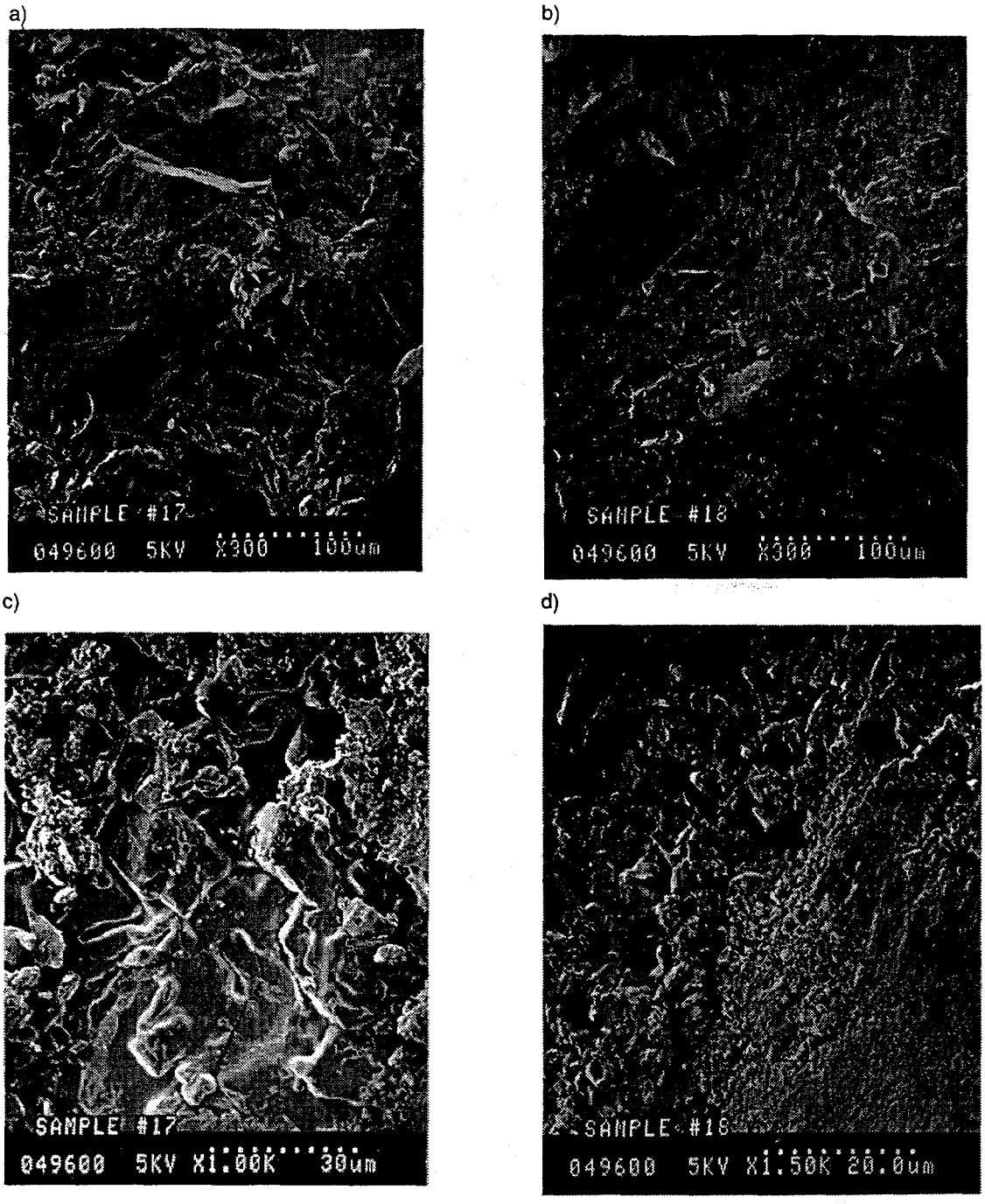

Fig 5. SEM photographs of PBX 9501. a) and c) are from a pellet heated to 180 °C and then cooled. Chemical analysis showed no significant decomposition. b) and d) are from a pellet heated as shown in Fig. 3. Chemical analysis indicated 5% decomposition of the HMX. Magnification scales are shown in each photograph.

DISCUSSION

The most obvious aspect of the data obtained in these experiments is the complex coupling of the chemical and physical processes that occur during heating of confined EM. Late-time decreases in load readings, such as that shown in Fig. 3, were observed for many of the materials studied, particularly those initially pressed to very high densities. These decreases may be due to void collapse under the increasing load generated by pressurization from product gases. This is not unexpected, but it leads to difficulty in analysis, particularly for deriving chemical reaction rates. With void volumes changing during decomposition it becomes difficult to derive reacted gas fractions from these experiments. Further discussion of detailed analysis is presented in reference 2. To gain additional insight into the thermal response of these EMs, we are developing a new experimental arrangement that will allow the top piston of the hot cell to move and to measure its displacement. We believe that a combination of data from the present fixed- volume/variable-load experiments with those from the new fixed-load/variable-volume experiments will help us to decouple some of the mechanical and chemical responses.

The morphology changes observed in the postmortems may significantly affect performance of these thermally degraded materials. The SEM results in Fig. 5b show a significant number of voids formed relative to the baseline material. Also, Fig. 5d shows a large network of connected porosity. It appears that the binder has been depleted leaving open paths for flame propagation and significant surface area for enhanced burning. The result may be accelerated burn rates, increased sensitivity, and greater violence-of-reaction. It would, of course, be preferable to investigate morphological changes in real time rather than relying on postmortem examination because voids and cracks could be formed during the cool-down period. We are investigating the potential utility of an ultrasonic probe to monitor EM density in real time during the heating process.

At this time we intend to continue to focus attention on pure HMX. There are indications that phase transitions may be dependent on particle size [3], and we are therefore going to perform new experiments with pellets pressed from powders with narrow distributions of particle size. In addition we will perform more complete and quantitative postmortem examinations of the heated materials.

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