Identification test of elements remaining in the barrel after firing, using Differential Scanning Calorimetry

A Plachá\textsuperscript{1,2}, P Prasula\textsuperscript{1} and J Rečko\textsuperscript{1}

Military Institute of Armament Technology, Zielonka, Poland

E-mail: plachaa@witu.mil.pl

Abstract. The issue of elements remaining in the barrel after firing is crucial both for the safe use of munition, and its reliability. These elements may be categorized as being part of a metal case or a projectile (for example, fragments of broken connectors between a metal band and a projectile), or those associated with a propelling charge (like unburnt propellant grains). Both groups are undesirable and reflect the ammunition improper work. During own shooting tests of a 120 mm mortar ammunition the problem of unburnt elements remaining in the barrel occurred. The collected material was tested using one of the thermal analysis techniques - Differential Scanning Calorimetry - to characterize and to identify the tested sample.

1. Introduction

Military Institute of Armament Technology specializes in design and tests of various types of artillery ammunition, include 120 mm tank ammunition \cite{2,3,4,5,6} and 120 mm mortar ammunition \cite{1}. During the shooting tests of a 120 mm mortar ammunition, carried in Military Institute of Armament Technology, the problem of unburnt elements remaining in a barrel occurred. The unknown elements found after shooting had a cylindrical shape, length range between 10-18 mm and its structure were similar to the structure of epoxy-based resin. The elements have been presented on the figure 1.

The presence of such elements is of an utmost importance for operation safety and the reliable performance of ammunition. Taking this into consideration, the decision was made to identify the elements remaining in the barrel after firing using Differential Scanning Calorimetry.
2. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a measurement technique based on the difference in the amount of energy delivered to the test and reference samples. Both samples are placed in crucibles and then heated, maintaining nearly identical conditions, according to the fixed rate of temperature rise $\beta$. The crucibles with the test sample and the reference sample, which usually is an empty crucible, are placed in two different sockets in the measurement container of the calorimeter. They are heated throughout the experiment simultaneously, maintaining the temperature difference as low as possible and close to zero. When the test sample exceeds its maximum temperature limit - it ignites, and as a result, the thermal balance between the two crucibles is disrupted. The control mechanism detects the temperature difference and begins a compensating process using a heater, which supplies as much energy to the sample with lower temperature as required to equal the temperature difference between the crucibles, and as such, detects the enthalpy change of the tested sample [7]. The DCS test results in a thermal curve, as a function of energy versus temperature, on which several noticeable phases of the heating process can be distinguished:

- phase one – shaping the base line,
- phase two – beginning of the process,
- phase three – maximum pace of the process reached; peak maximum,
- phase four – restoring balance.

Each calorimetry measurement provides qualitative and quantitative data. The most relevant qualitative data are:

- the number of endo- or exothermic effects,
- peak shape: sharp or distorted. The former indicates a constant temperature change, while the latter displays a specific range of temperatures during the change,
- peak variations with a change of measurement conditions [8].

The most relevant quantitative data possible to derive out of the thermal curve are:

- peak onset, defining the temperature of the emission or absorption of energy by the examined material,
- peak end, which may indicate the end of the change,
- peak maximum, defining the temperature at which the process pace is fastest,
- surface area beneath the peak, which allows to determine the total energetic effect (enthalpy) of the change,
- peak symmetry, which provides data about the amount of energy released before and after reaching its maximum [8].

3. Differential Scanning Calorimetry

3.1. Test object

The thermal analysis was performed on a referential sample, shown in the figure 1 and substances used for the production of the 120 mm mortar rounds: ignition cartridge propellant, propellant charge, high-energy adhesive, two-component methacrylate adhesive, and two-component epoxy-based resin. The results, presented in the figures 2-5, were compared with the referential sample. The determined values of the parameters characterising physical and chemical transformations were collated in table 1.

3.2. Test conditions

The test was performed using a TA Instruments DSC Q100 device. The measurement was done in an inert atmosphere, filled with a non-reactive nitrogen. The temperature raise rate was $10 \, ^\circ C / \text{min}$,
and the test temperature range was 20 – 500 °C. Non-hermetic aluminium crucibles were used for measurement, and the amount of the samples tested ranged from 0.6 mg to 1.0 mg.

3.3. Test results
Thermograms, obtained after testing the samples described in section 2.1, produced data for the determination of the peak’s maximum temperature (Tmax) at which the process pace is fastest, onset temperature (Tonset), at which the change is initiated, and the reaction energy (Q), which is the surface area beneath the peak. The thermograms of the tested materials are presented below.

Table 1. Exothermic proces parameters

| Sample | Exothermic process I | Exothermic process II |
|--------|----------------------|-----------------------|
|        | T_onset (°C) | T_max (°C) | Q (J/g) | T_onset (°C) | T_max (°C) | Q (J/g) |
| Ignition cartridge propellant | 183.9 | 206.2 | 3156 | - | - | - |
| Propellant charge | 188.2 | 193.6 | 2082 | 233.9 | 224.7 | 117.4 |
| High-energy adhesive | 196.3 | 206.4 | 2670 | - | - | - |
| Two component epoxy-based resin | - | - | - | - | - | - |
| Two-component methacrylate adhesive | - | - | - | - | - | - |

3.3.1 Referential sample
Referential sample thermogram, presented in the figure 1, shows a slightly increasing exothermic effect during the heating process. The exothermic process occurs above 250 °C, with a very low exothermic effect, which proceeds to material breakdown and has the highest rate at 208.7 °C. Above this temperature, as heating continues, another process with a little energetic effect occurs, which proceeds to material breakdown and has the highest rate at 208.7 °C. Next, above the given temperature, another material breakdown occurs. It is exothermic, most probably connected with the further breakdown and oxidation of the charred substance (and carbon). The tested material is a mix of unknown substances.
3.3.2 Ignition cartridge propellant sample

Propellant from ignition cartridge breakdown occurred in a typical manner to other high-energy materials. The thermogram, presented in the figure 2, shows one, narrow exothermic peak. The material breakdown occurs above 150 – 160 °C, and has the highest pace at 206 °C. The energetic effect of the tested material is far greater than the referential material.
3.3.3 Propellant charge sample
Propellant charge breakdown occurs similarly to the ignition cartridge propellant. The thermogram, presented in the figure 3, shows a relatively narrow, exothermic peak, with the maximum breakdown point at 193.6 °C, which means that the sample was highly energetic. Above this temperature, another exothermic, low energetic effect occurs, which may be related a secondary reaction of the breakdown products.

![Propellant charge thermogram](image)

**Figure 3.** Propellant charge thermogram

3.3.4 High-energy adhesive sample
The high-energy adhesive breakdown was typical of high-energy materials. During the heating process, the material remains stable. On the thermogram, presented in the figure 4, one intense, narrow, exothermic peak can be observed. The material breakdown occurs above 150 – 160 °C and has the highest pace at 206.4 °C. The energetic effect of tested material is far greater than the referential material
3.3.5 Two-component epoxy-based resin sample
The two component epoxy-based resin, presented in the thermogram, presented in the figure 5, lacks a characteristic peak when it reached 208 °C, unlike the referential sample. The material, when tested above ca. 50 °C, reaches a deflection temperature, beyond which the resin starts to take the form of plastic. This process is associated with a minor endothermic effect. A high energetic increase of the process can be observed when the temperature reaches ca. 200 °C, which is related to the breakdown of the tested material.

Figure 4. High-energy adhesive thermogram

Figure 5. Two-component epoxy-based resin thermogram
3.3.6 Two-component methacrylate adhesive sample

The two-component methacrylate adhesive thermogram, presented in the figure 6, shows many physical and chemical transformations. The associated effects are endothermic. The tested material behaved entirely differently in comparison to the referential sample.

![Figure 6. Two-component methacrylate adhesive thermogram](image)

4. Conclusions

The Differential Scanning Calorimetry test cannot clearly identify the material of the referential sample. The test revealed some similarities between the referential sample and the high-energy adhesive and the ignition cartridge propellant, because both samples have a characteristic, intense breakdown peak at 208 °C; however, the energetic effect of the high-energy adhesive and the ignition cartridge propellant is far greater than the referential sample, and so it cannot be stated that the latter was made up entirely of one the above-mentioned substances. In addition, the referential sample thermogram, presented in the figure 1, on the right side, further than the temperature peak, depicts a shift in the curve that indicates a further breakdown of the sample accompanied by an exothermic effect. Presumably, this effect is related with the transformation of carbon substances and their oxidation or breakdown. One can make an assumption that those were remnants of the unburnt high-energy adhesive, or the ignition cartridge propellant, or both substances combined, with the combustion products or mixed combustion products of those substances. In order to fully qualitatively identify the referential sample, one should perform additional tests, such as infrared spectrometry or elementary analysis.

5. References

[1] R. Kostrow, M. Magier, Z.Pankowski, ,,Artyleria XXI wieku”, WITU, Warszawa, 2006
[2] Kuśnierz T Ammunition with High Explosive – fragmentation projectiles for Leopard tanks used by the Polish Army, Issues of Armament Technology, 1-2012
[3] Motyl, K.; Magier, M.; Borkowski, J.; Zygmunt, B. Theoretical and experimental research of anti-Tank kinetic penetrator ballistics. *Bulletin of the Polish Academy of Sciences: Technical Sciences* 2017, 65(3), 399–404. DOI: 10.1515/bpasts-2017-0045

[4] Magier, M. The conception of the segmented kinetic energy penetrators for tank guns. *Journal of Applied Mechanics, Transactions ASME* 2010, 77(5), 1–10. DOI: 10.1115/1.4001714

[5] Kruszka, L.; Magier, M.; Zielenkiewicz, M. Experimental analysis of visco-plastic properties of the aluminum and tungsten alloys by means of hopkinson bars technique. *Applied Mechanics and Materials* 2014, 556, 110-115. DOI: 10.4028/www.scientific.net/AMM.566.110

[6] Kruszka, L.; Magier, M. Experimental investigations of visco-plastic properties of the aluminum and tungsten alloys used in KE projectiles. *The European Physical Journal Web of Conferences* 2012, 26, 05005, DOI: 10.1051/epjconf/20122605005

[7] W. Przygocki, „*Metody fizyczne badania polimerów*”, PWN, Warszawa, 1990

[8] Z. Sierpiński, *Wykłady z przedmiotu „Instrumentalne metody badawcze*”, AGH, Kraków