The application of microcalorimetry in the compatibility test for pyrotechnics ☆

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Abstract

This paper describes the characteristics of the microcalorimeter and method used in compatibility tests for pyrotechnics. The results are compared with those of the traditional VST method. To demonstrate the accuracy of the results, we analysed the surface structure of the tested materials using SEM. The testing conditions using the microcalorimetry method approach the actual storage conditions more than in the other methods, and the conclusion based on microcalorimetry is more reliable than that of traditional methods.

Keywords: Compatibility test; Microcalorimeter; Pyrotechnics; SEM

1. Introduction

Because of their particular structure and high sensitivity, microcalorimeters can be used in many fields. This article introduces their application to the compatibility test for pyrotechnics.

Thermal decomposition, affecting the processes by which products are manufactured, used and stored, plays a very important part in the compatibility test.

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Pyrotechnics consist of organic compounds, organometallic salts and metal powder. Actually, there is a binding of the metal atoms preventing ready gasification, while most pyrotechnics are decomposed by heat. Because some substances produce little gas or nothing at all during tests, the classical vaccuum stability test (VST) method cannot be used in these cases. Using the microcalorimetric method, we can measure the heat changes. Therefore, the statement above is an important condition of the microcalorimetry method over the traditional gas method.

However, most pyrotechnics react easily with the contacting materials because of their metallic ions. Therefore, their chemical incompatibility is very obvious. In fact,
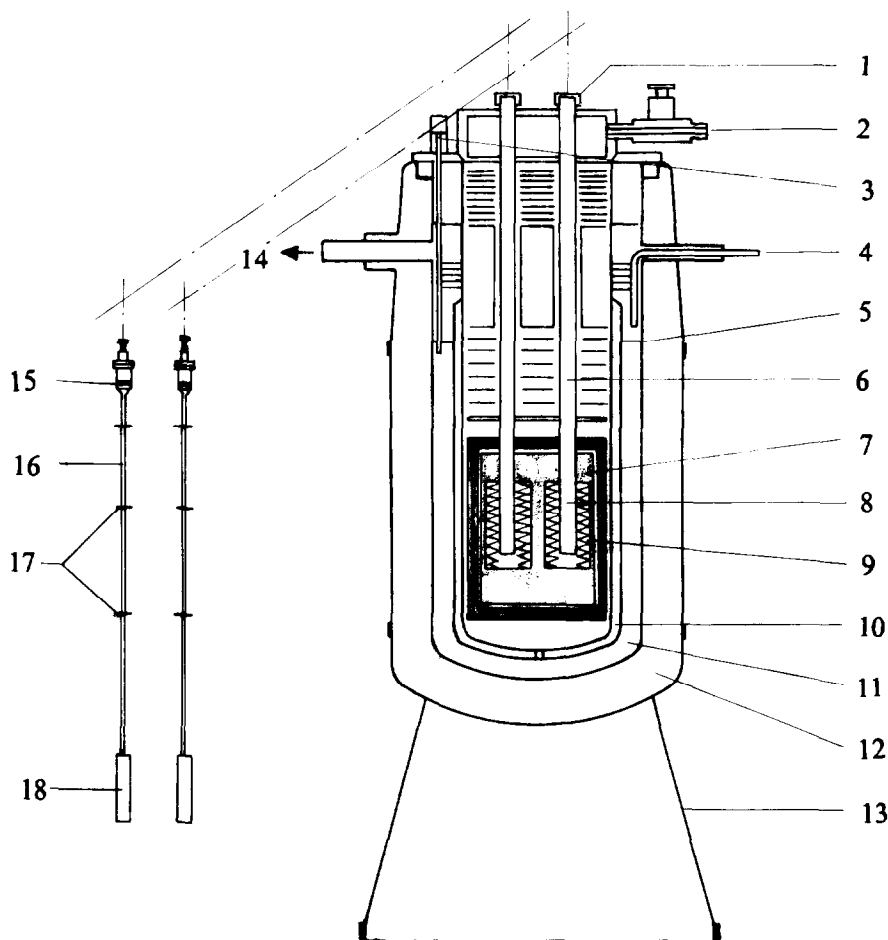

Fig. 1. Description of the microcalorimeter: 1, tight lid; 2, control of the environment; 3, level gauge; 4, liquid nitrogen inlet; 5, nitrogen level; 6, access hole; 7, calorimetric block; 8, energy monitoring space; 9, heat flux transducer; 10, tight container; 11, nitrogen tank; 12, insulation; 13, support; 14, outlet; 15, tightness; 16, connection; 17, screens; 18, vessel.
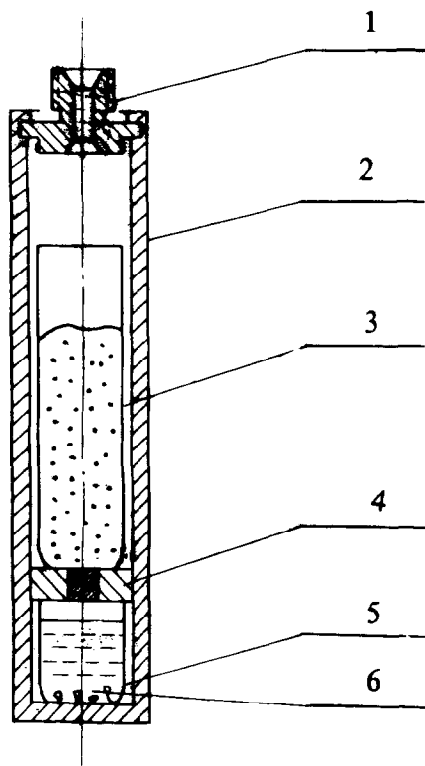
Fig. 2. Calorimetric vessel: 1, tight lid; 2, container; 3, sample glass ampoule; 4, cross shelf; 5, humid glass ampoule; 6, saturated $KNO_3(aq.)$.

many reactions leading to incompatibles need water. And in their storage, the water in air affects the stability and compatibility of pyrotechnics. The traditional test methods all overlook the influence of humidity. Microcalorimetry can test the compatibility of the samples under more humid conditions. This is another advantage of the microcalorimetry method.

Therefore, as a new thermal analytical method used in the compatibility test for pyrotechnics, microcalorimetry can provide accurate and reliable results [1,2].

2. Apparatus

The Calvet low-temperature microcalorimeter, with the configuration shown in Figs. 1 and 2, works by means of heat conduction. Inside the microcalorimeter, heat exchange takes place between the calorimetric vessel and the environment, its quantity being measured by a heat flux transducer consisting of 496 thermocouples.

The quantity of heat exchanged is recorded as a heat flow rate curve and recorded as thermal power in W.
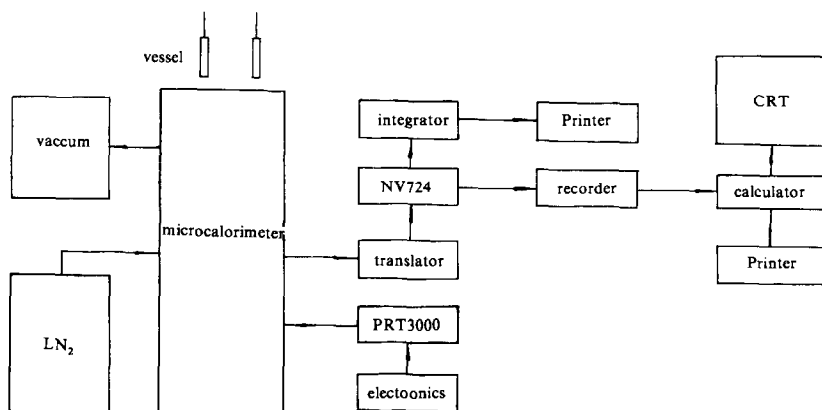
Fig. 3. Flow chart of the microcalorimeter.

The quantity of heat produced by the system Q is not measured directly by the microcalorimeter but the momentary thermal power produced during the process is recorded. W is a continuous function of time (t)

$$W = f(t) \qquad (1)$$

The integrated value of Eq. (1) is the heat Q produced during the process.

The working flow chart of the microcalorimeter is shown in Fig. 3. The main part of the calorimeter consists of a thermostated block placed inside a cooled enclosure. A temperature is chosen either a constant value or scanned at slow rate. When a lower temperature is required, liquid nitrogen is introduced into the nitrogen tank with the temperature being decreased to a lowest value of $-196°C$. The temperature of the thermostated block is adjusted by a PRT3000 temperature controller; the signal of the heat-flux transducer is amplified by an NV724 millivolt amplifier, fed into a recorder and calculated by a computer.

3. Experimental

The temperature of the instrument is raised according to the program and maintained at a constant value. The baseline of the instrument is measured using an α-Al_2O_3 standard.

When the baseline is stable, the pyrotechnics or contacting materials or a 1 : 1 mixture of pyrotechnics and contacting materials is placed in the sample vessel, and their heat flow rate curves are measured. The test time of each sample is 40 h.

When the compatibility test needs to take place under humid conditions, a quantitative amount of saturated KNO_3 solution is added to the sample and reference vessels. When the relative humidity in the vessel reaches 90%, the baseline

and heat flow rate curves of the pyrotechnics, contacting materials, and 1:1 mixture are measured. The test time of each sample is 120 h.

The standard of the microcalorimetry method for judging compatibility is as follows. The theoretical heat flow rate curve is a new heat flow rate curve obtained by adding the heat flow rate curves for pyrotechnics and for contacting materials. The actual heat flow rate curve is a heat flow rate curve of a mixture (1:1 wt) of pyrotechnics and contacting materials.

(a) When the actual heat flow rate curve is lower than the theoretical heat flow rate curve, the system is considered to be compatible.
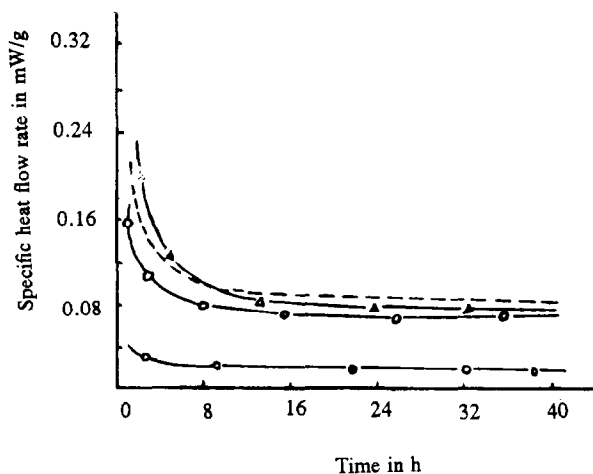

Fig. 4. The heat compatibility of HG(NT)$_2$ and RDX: ○, Ag(NT)$_2$; □, RDX; △, 1 g Hg(NT)$_2$ + 1 g RDX; – – –, theoretically non-reacting.
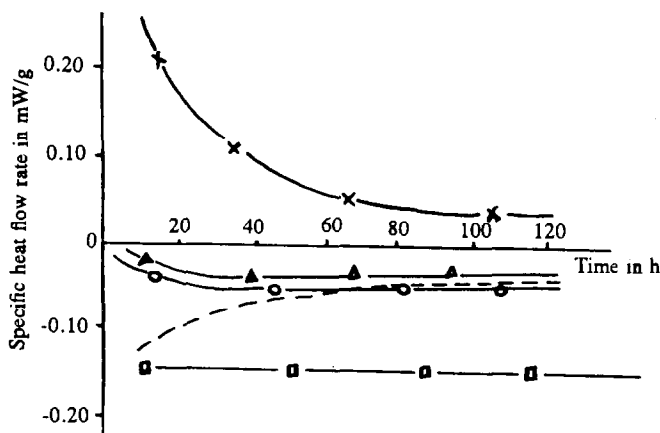
Fig. 5. The compatibility of CP and Al and Cu under humid conditions: ×, CP; ○, CuAl; △, CP + Al; □, Cl + Cu; – – –, theoretically non-reacting.
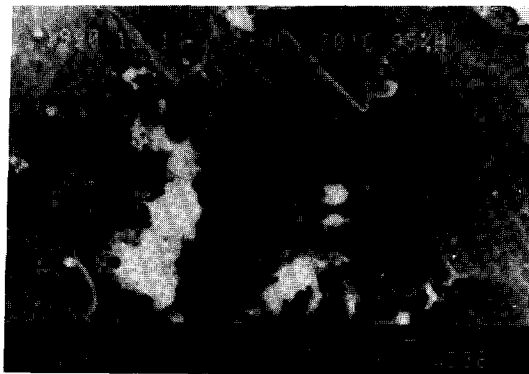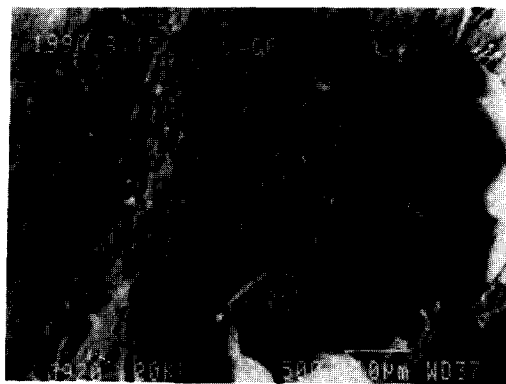
Fig. 6. Scanning electron micrograph of Al.

Fig. 7. Scanning electron micrograph of Cu.

(b) When the actual heat flow rate curve is higher than the theoretical heat flow rate curve, and less than 1.5 times the theoretical heat flow rate curve, the system is considered to be incompatible, having a slight reaction.

(c) When actual heat flow curve rate is higher than 1.5 times the theoretical heat flow rate curve, the system is considered to be incompatible.

4. Results and discussion

Using the microcalorimetry method, the thermal compatibility between $Hg(NT)_2$ and cyclotrimethylene trinitramine (RDX) was determined and the results are shown in Fig. 4. The experimental conditions were 100°C and 40 h. Obviously, the actual heat flow rate curve is lower than the theoretical heat flow rate curve: this system is compatible. This result is identical with that obtained by VST. In VST,

the volumes of gases produced at 100°C were: HG(NT)$_2$, 0.19 ml g^{-1}: RDX, 0.25 ml g^{-1}; the mixture, 0.16 ml g^{-1}. The system is compatible.

Using the microcalorimetry method, the compatibility between 2-(5-cyanotetrazolato)pentaaminocobalt(III)perchlorate (CP) and Al and Cu was tested at 50°C and 90% relative humidity for 120 h. The results are shown in Fig. 5. The actual heat flow rate curve of the mixture of CP and Al is lower than the theoretical heat flow rate curve, so CP and Al are considered compatible. This result is identical with that of VST. The actual heat flow rate curve of the mixture of CP and Cu is higher than the theoretical heat flow rate curve but less than 1.5 times the theoretical heat flow rate curve, so the system is considered to be incompatible, having a slight reaction. This result is different from that of VST. In VST, the volumes of gases produced were: CP, 0.11 ml g^{-1}; Cu, 0 ml g^{-1}; the mixture, 0.09 ml g^{-1}. The system is compatible. The surfaces of Al and Cu were analysed using SEM after the compatibility tests. The results are shown in Figs. 6 and 7. The surface of Al is not corroded, but there are corroded spots on the surface of Cu, forming honeycomb pores. The analytical SEM results prove that the microcalorimetry method enables us to know not only the changes in the properties of pyrotechnics, but also changes in the properties of contacting materials. The results from microcalorimetry are more reliable.

Using the microcalorimetry method, the compatibility between B-KNO$_3$ primary ignition composite and Cr, Mo steel was tested at 70°C, under humid conditions, for 120 h. The results are shown in Fig. 8. The actual heat flow rate curve is more than 1.5 times the theoretical heat flow rate curve, so that the system is incompatible. This result is different from that of VST. In VST, the volumes of gases produced were: B-KNO$_3$ primary ignition composition, 0.13 ml g^{-1}; Cr, Mo steel, 0 ml g^{-1}; the mixture, 0.08 ml g^{-1}. This system is considered to be compatible by VST. But analysis of the B-KNO$_3$ primary ignition composite using DTA showed
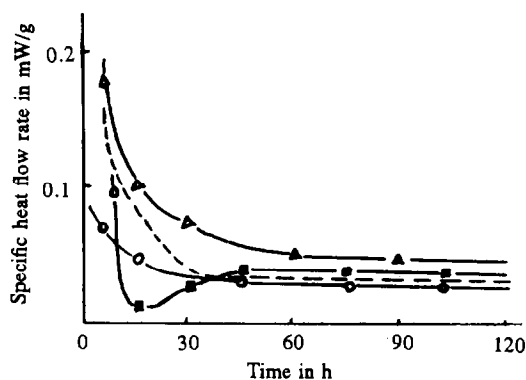

Fig. 8. The compatibility of B-KNO$_3$ primary ignition composition and Cr, Mo steel under humid conditions: ○, B-KNO$_3$ primary ignition composition; □, CrMo steel; △ 1:1 mixture; – – –, theoretically non-reacting.

its weight being increased by 2.7% after the exothermic peak at 550°C. The DTA measurement was at a heating rate of 10°C min^{-1}. Therefore, B-KNO$_3$ primary ignition composite did not produce any gases. So the VST result is not accurate.

5. Conclusions

Microcalorimetry as a new analytical method for the study of pyrotechnics compatibility can meet the demands of temperature, humidity and precision. Firstly, the instrument has high sensitivity. Compatibility test experiments may be carried out at 50–100°C or even lower, with extended curves being obtained. Secondly, the sample vessels are larger, and a humid condition can be maintained thus making the results more reliable. Thirdly, physical and chemical changes always take place with thermal changes. Therefore, the microcalorimetry method is superior, without the shortcomings of the traditional method.

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