PREDICTION OF THE THERMAL BEHAVIOUR OF ENERGETIC MATERIALS BY ADVANCED KINETIC MODELLING OF HFC AND DSC SIGNALS

Bertrand Roduit[1], Patrick Folly[2], Alexandre Sarbach[2], Beat Berger[2], Michael Ramin[3], Beat Vogelsanger[3]

[1]AKTS AG Advanced Kinetics and Technology Solutions, http://www.akts.com, TECHNOArk 3, 3960 Siders, Switzerland
[2]armasuisse, Science and Technology Centre, http://www.armasuisse.ch, 3602 Thun, Switzerland
[3] Nitrochemie Wimmis AG, http://www.nitrochemie.com, 3752 Wimmis, Switzerland

Abstract

High energetic materials can slowly decompose during storage or transport particularly at elevated temperatures which may result in reduced performance and correct functionality. Even very low decomposition progress of the exothermic reaction resulting in minor heat release can significantly change the properties of the propellants leading to shortening of the service life-time. The reaction progress influencing already the behaviour of the samples can be in the range of ca. 1-2% of the total decomposition degree. There are the literature reports showing that the amount of the evolved heat during decomposition as low as ca. 40 J/g can alter the material properties. Monitoring such a minor heat release requires very sensitive techniques as Heat Flow Calorimetry (HFC).

Proposed method for simulation of the amount of heat evolved during aging of the energetic materials which allows predicting the thermal behaviour of the samples is based on the elaboration of the difference between the HFC signals recorded for the unaged and differently altered samples. The samples aged in furnaces at 50, 60 and 70°C were investigated by HFC technique at 80°C and obtained signals were compared with the traces of the unaged sample recorded during 10 days also at 80°C. Observed changes of the recorded heat flows as a function of time at 80°C for the differently aged samples related to the heat flow of the unaged sample allowed the determination of the kinetic parameters of the decomposition process. They were determined by the differential isoconversional method applying the principle of the compensation effects widely used in the kinetics of the solid heterogeneous reactions. The knowledge of the kinetics of the early stage of the process allowed the precise prediction of the reaction rate at any temperature mode. It allowed also the simulation of arbitrarily chosen cumulative heat release (e.g. 40 J/g) at any temperature profile such as storage conditions depicted in STANAG 2895 or A1 cycles "extreme hot climate" with daily temperature fluctuations between 32 and 71°C.

The application of the proposed advanced kinetic method of the elaboration of the HFC signals significantly shortens the time of the experiments: note that the required information is gained from the HFC experiments carried out at relatively high temperature of 80°C.

1. Introduction

The methods of the simulation of the aging of any materials i.e. the prediction of the changes occurring in the samples due to exposure to the higher than ambient temperatures are relatively well elaborated when large amount of reaction progress is taken into consideration. There are numerous papers describing the application of commonly used DSC methods, see e.g. publications of the present authors [1-2]. The situation is much more complicated in the case of the energetic materials which often decompose with very long induction period. The very minor changes of the decomposition progress can result in the significant altering of their thermal behaviour, its service life-time and the ballistic properties. For these materials the very small thermal effects have to be measured and/or simulated because even so low amount of evolved heat as 40 J/g [3] can, as a one among other physicochemical parameters, indicate the progress of the aging which changes their properties. This amount of the heat evolved during beginning of the exothermal decomposition amounts to ca. 1-2% of the total heat of the reaction. Such a small thermal effects cannot be sufficiently monitored by commonly applied DSC systems: the interpretation of the first 1-2% of the decomposition is very difficult by DSC due to (i) its low intensity and, more important (ii) due to the problems of the base-line construction which significantly influences the determination of the integral intensities of the recorded heat flows, especially at the beginning of the experiment.

Heat Flow Calorimetry (HFC) is a sensitive technique allowing monitoring very small heat flows, however, its drawback lays in a very time consuming collection of the experimental data. The determination of the kinetics of the decomposition of the energetic materials by HFC requires experiments at least 3-4 temperatures and hardly can be achieved in the reasonable time-scale. The problem can be partly overcome by the combination of the HFC (at very low reaction progress α values) and DSC (for higher α). Details of such a procedure are given in [4].

In the present paper we report the new method of the simulation of the minor heat release occurring during aging of the energetic materials. The method is based on the application of the only HFC signals recorded at the same temperature for the fresh and in controlled way altered samples. The comparison of the shape and the position on the time scale of the fresh and aged samples allows the determination of the kinetics of the very early stage of the decomposition. The knowledge of the kinetic parameters of the decomposition will allow simulation of the reaction progress and, in turn, the cumulative heat release under any temperature mode.

2. Experimental

The decomposition of a double base propellant for small calibre applications has been studied by HFC using the following procedure:

(1) Before the HFC measurements the samples were exposed in furnaces to the temperatures of 50, 60 and 70°C for 4, 8 and 12 weeks.

(2) After 4, 8 and 12 weeks of aging the 3.0 g samples were measured by Heat Flow Calorimetry in a Thermal Activity Monitor (TAM) calorimeter at 80°C. The experiments were carried out during 10 days. The total amount of evolved heat (cumulative heat release) for the unaged sample reached the value of 45.533 J/g. This value has been used for the determination of the "HFC monitored reaction progress" which varied between 0 (for the amount of evolved heat equal to 0.0 J/g) and 1 (if the cumulative heat evolved amounted to 45.533 J/g). It is necessary to keep in the mind that the amount of evolved heat during total decomposition measured by DSC is equal to ca. 3090±220 J/g. Therefore the real reaction progress achieved during HFC experiments is in the range of ca. 0.012-0.014 only.

(3) The fresh, unaged sample, used as a reference for the kinetic calculations, was measured by HFC also at 80°C.

The HFC traces were elaborated by AKTS-Thermokinetics Software Version 3.10 [5] using the differential isoconversional method and the concept of the compensation effect commonly applied in the kinetics of the solid heterogeneous reactions [6-7].

3. Results and kinetic analysis

The measured heat flow signals at 80°C after aging at 50, 60 and 70°C for several periods of time are shown in the Fig.1. When compared with the unaged propellant, the heat flow signals of the aged samples shift to left, towards shorter times. This shift is the consequence of preliminary thermal ageing which results in the shortening of the induction period [8-10]. The amount of unmeasured heat evolved during aging is proportional to the reaction progress and depends on the kinetic parameters of the reaction (activation energy E and the pre-exponential factor A) and, additionally, on the thermal history of the sample during aging (temperature and time). Knowing exactly the thermal history during aging, one can use the observed shift of the heat flow signals for determination of the kinetics of the early stage of decomposition. The basic concept of the kinetic analysis is presented below.
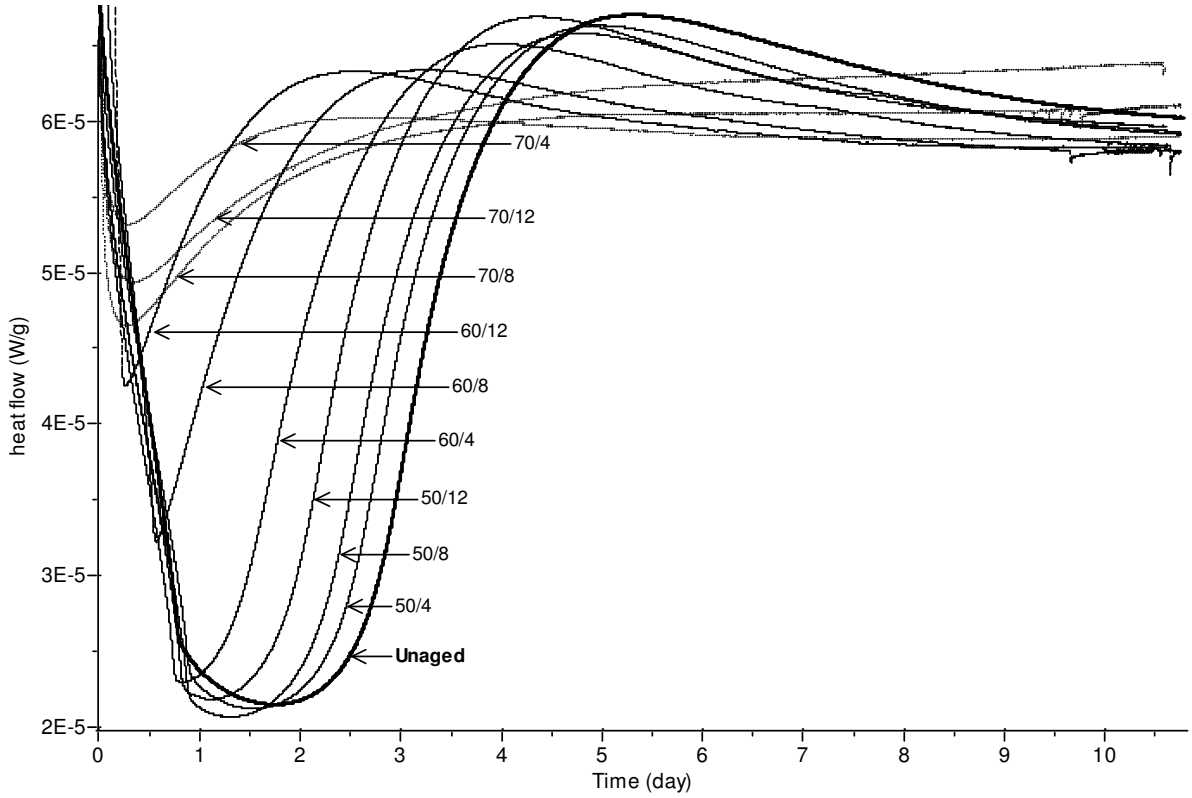
Fig.1 Heat flow signal at 80°C of the fresh sample (bold line) and after thermal aging. The numbers placed on the curves depict the temperature (in °C) and duration of the aging (in weeks).

4. Basic principle of the kinetic analysis of the HFC signals

As it has already been mentioned in the Experimental section, the kinetic analysis has been performed only for the narrow range of the decomposition progress i.e. only for this one which has been monitored by HFC. Therefore, the expression "reaction progress α" applied throughout the text means the "HFC monitored reaction progress α" expressed by relating the amount of evolved heat to the maximal value of cumulative heat release obtained in HFC measurements i.e. to 45.533 J/g.

Assuming that the reaction rate $d\alpha/dt$ at a given reaction progress α is only a function of the temperature, a differential isoconversional analysis [5, 11] can be performed to obtain a precise kinetic description of the early stage of the reaction measured by HFC. The reaction rate can be expressed as:

$$\frac{d\alpha}{dt_\alpha} = A(\alpha)\exp(-\frac{E(\alpha)}{R}\frac{1}{T(t_\alpha)})f(\alpha) \tag{1}$$

where t_α, $T(t_\alpha)$, $E(\alpha)$ and $A(\alpha)$ are the time, temperature, apparent activation energy and preexponential factor, at conversion α, respectively, and $-E(\alpha)/R$ and $ln(A(\alpha) \cdot f(\alpha))$ are the slope and the intercept with the vertical axis of the plot of $ln(d\alpha/dt)$ vs. $1/T(t_\alpha)$ and where $f(\alpha)$ depicts the differential form of the function of the reaction progress α depending on the reaction mechanism. The equation of reaction rate can be rewritten in logarithmic form:

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = \ln(A(\alpha)\cdot f(\alpha)) - \frac{E(\alpha)}{R}\frac{1}{T(t_\alpha)} \tag{2}$$

Based on the so-called 'compensation effect' (see e.g. the papers describing the compensation behaviour in solid-state decomposition [6] or discussing the significance of "compensation effect" [7] in solid state-kinetics) between the activation energy and the pre-exponential factor, it can be assumed that the following ratio C remains constant

$$\frac{\ln(A(\alpha)\cdot f(\alpha))}{E(\alpha)} \cong C \tag{3}$$

therefore

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = E(\alpha)\cdot(C - \frac{1}{R\cdot T(t_\alpha)}) \tag{4}$$

Finally, the heat flow rate at any new temperature profile $T(t_\alpha)$ can be obtained as following:

$$\frac{dQ}{dt} = Q_{r,\max \ Unaged \ at \ 80°C} \frac{d\alpha}{dt_\alpha} \tag{5}$$

where

$$Q_{r,\max \ Unaged \ at \ 80°C} = -45.533 \ J/g$$

is the maximal value of the cumulative measured heat release of the unaged propellant recorded at 80°C for 10 days, and

$$\frac{d\alpha}{dt_\alpha} = \exp(E(\alpha)\cdot(C - \frac{1}{R\cdot T(t_\alpha)})) \tag{6}$$

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{\exp(E(\alpha)\cdot(C - \frac{1}{R\cdot T(t_\alpha)}))} \tag{7}$$

$$\text{and } E(\alpha) = \frac{\ln(\frac{d\alpha}{dt_\alpha})_{unaged \ at \ 80°C}}{C - \frac{1}{R\cdot T_{80°C}}} \tag{8}$$

The numerical approximation of the parameter C can be done by comparing for the aged sample the shift and shape of the measured heat flow with its simulated course (eq. 5). The comparison of the HFC signal measured at 80°C for the sample previously aged at 50°C for 12 weeks with the simulated curve is presented in Fig. 2. The best fit was obtained for the value of $C = 0.000246\ mol/J$. The Fig.2 depicts additionally the heat flow recorded for the unaged sample at 80°C and the corresponding cumulative heat release for fresh and aged samples, respectively. It can be clearly observed that the experimental heat flow signal of the aged propellants is shifted towards shorter time when compared with the signal recorded for the unaged sample. During the approximation of the C value, its increase or decrease will also result in shifting heat flow signal towards longer or shorter times, respectively.
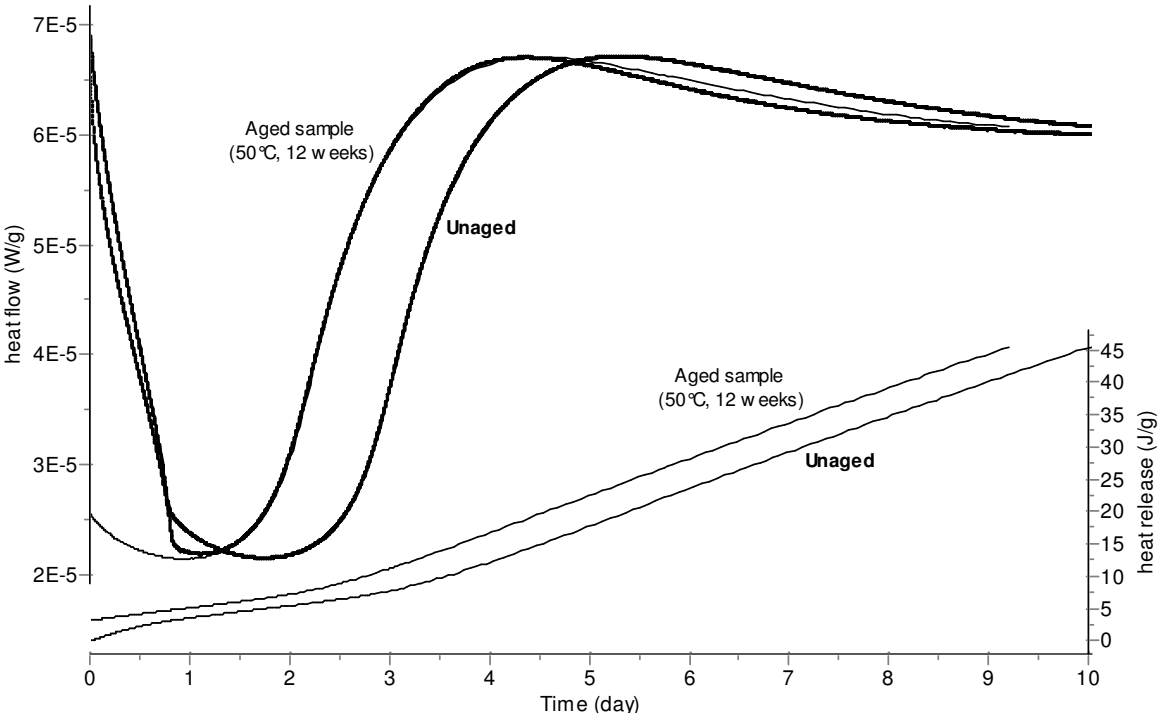

Fig.2 Experimental (bold) vs. simulated heat flow curves at 80°C of the unaged and aged (50°C, 12 weeks) propellant (top). Corresponding cumulative heat release curves are displayed at the bottom.

Once the optimum value for C is determined, the activation energy and the apparent pre-exponential factor can be calculated as a function of the reaction progress using the equations (8) and (3) and the results of such calculations are shown in the Fig. 3.
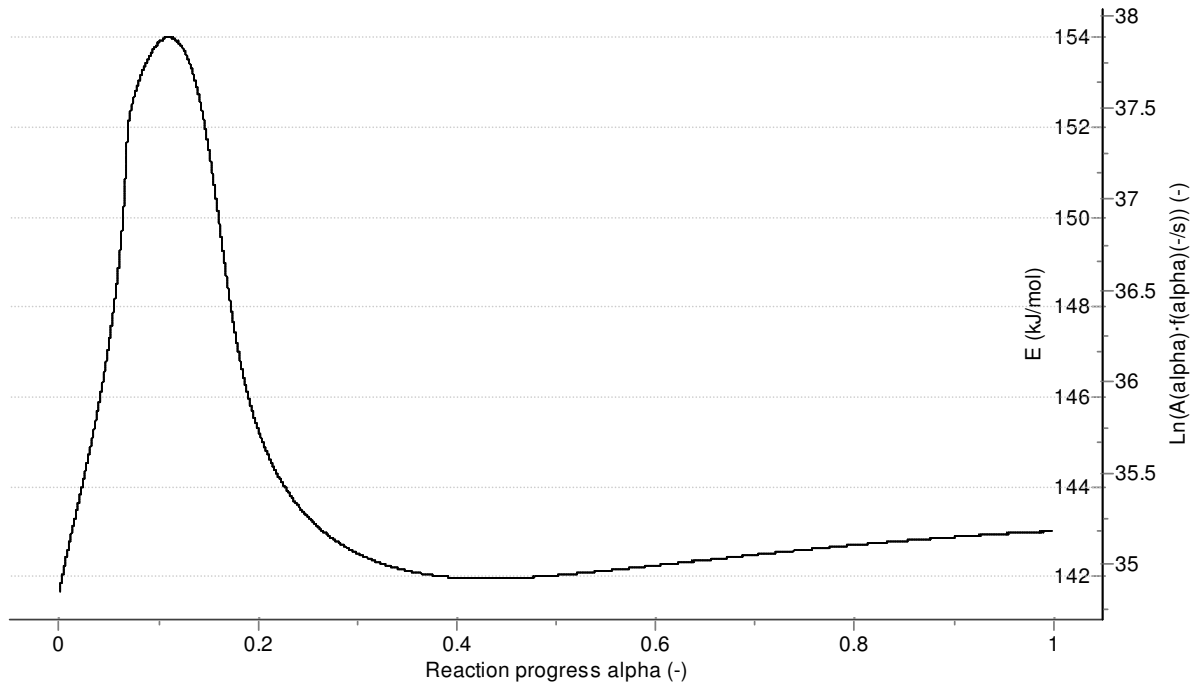
Fig.3 Activation energy *E* (kJ/mol) and pre-exponential factor in the form of the expression $A(\alpha) \cdot f(\alpha)(s^{-1})$ for the reaction of the propellant decomposition calculated from the heat flow signals monitored at 80°C during 10 days. At the end of the experiment the reaction progress is assumed to be 1 (see Experimental section). The calculations were done using the differential isoconversional analysis.

The reaction rate can be expressed at any temperature profile *T(t)* using eq. (6) and the time or temperature of the propellant aging can be obtained after numerical integration:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{A(\alpha) f(\alpha) \exp(-\dfrac{E(\alpha)}{R} \dfrac{1}{T(t_\alpha)})} \tag{9}$$

It is worth to underline that the kinetic parameters were calculated from the experimental data obtained in a very narrow range of the reaction progress. Therefore, the correct simulation of the amount of the evolved heat based on the reaction kinetics can be applied only if the maximal value of the cumulative heat release does not exceed the arbitrarily chosen value of 45.533 J/g. Any attempt to predict the course of the heat flow signals or amount of heat released which is larger than maximal measured value may result in uncertain results. If the simulation of the larger amount of heat is required then the range of the HFC experimental domain has to be extended up to higher temperatures or longer monitoring times.

5. Simulation of the thermal aging progress

The important goal of the investigation of the kinetics of the thermal decompositions of propellants is the possibility of determining time range over which the substance does not reach a

certain limit of decomposition progress which can be monitored e.g. by measuring cumulative heat release. During production, storage or final usage, the propellants are often exposed to temperature fluctuations. Due to the fact that the reaction rate varies exponentially with the temperature it is important to simulate the reaction progress in the real conditions, as a small temperature change can result in a significant increasing reaction rate. Since the HFC techniques can be used for recording very precisely the early stage of the decompositions at moderate temperatures, the reaction kinetics derived from HFC measurements can be applied for calculating very precisely the amount of heat release at any temperature mode such as stepwise variations, oscillatory conditions, temperature shock, or real atmospheric temperature profiles.

One of very interesting feature of the presented method is its ability of posterior determination of the reaction progress reached by propellants. After the determination of the kinetics from the series of the experiments presented in Fig.1 the reaction rate (expressed by the heat flow) and reaction progress (expressed by the cumulative heat release from 0 up to 45.533 J/g) of all aged samples at the point of the beginning of the HFC run at 80°C can be calculated for all storage temperatures and time periods. The results of these calculations are presented in Table 1. The experimentally measured values of the heat release from the spherical double base propellant obtained in another study [12] are reported for comparison in the last column of the Tab.1. Presented results indicate the higher thermal stability of the propellant examined in the present study: note smaller amount of heat evolved at the same aging conditions.

Table 1. Calculated cumulative heat release during aging of the samples in different conditions. The amount of the heat evolved was calculated by multiplying the reaction progress α by the maximal heat release recorded in HFC experiment at 80°C during 10 days (45.533 J/g).
[a] after 42.45 days, [b] after 56 days, [c] after 82.8 days.

Aging conditions		Reaction progress	Calculated	Experimental
temperature	time	α	heat release, sample I	heat release, sample II
°C	weeks	-	J/g	J/g
50	4	0.0332	1.51	2.66
50	8	0.0557	2.54	4.20
50	12	0.0703	3.20	5.32
60	4	0.0930	4.23	5.96
60	8	0.1441	6.56	10.97
60	12	0.2594	11.81	23.29
70	4	0.5824	26.52	35.51
70	8	1.0000	45.533 [a]	82.92 [b]
70	12	1.0000	45.533 [a]	142.00 [c]

The prediction of the thermal behaviour of differently aged propellant samples is additionally displayed in the Fig.4 showing the results of the simulation of the heat flow signals (A) and cumulative heat release (B) occurring during 4 weeks storage in the furnaces at 50, 60 and 70°C followed by the HFC run at 80°C. Fig. 4C shows the comparison of the experimental and simulated data of the heat flow signals obtained for the aged samples at 80°C.
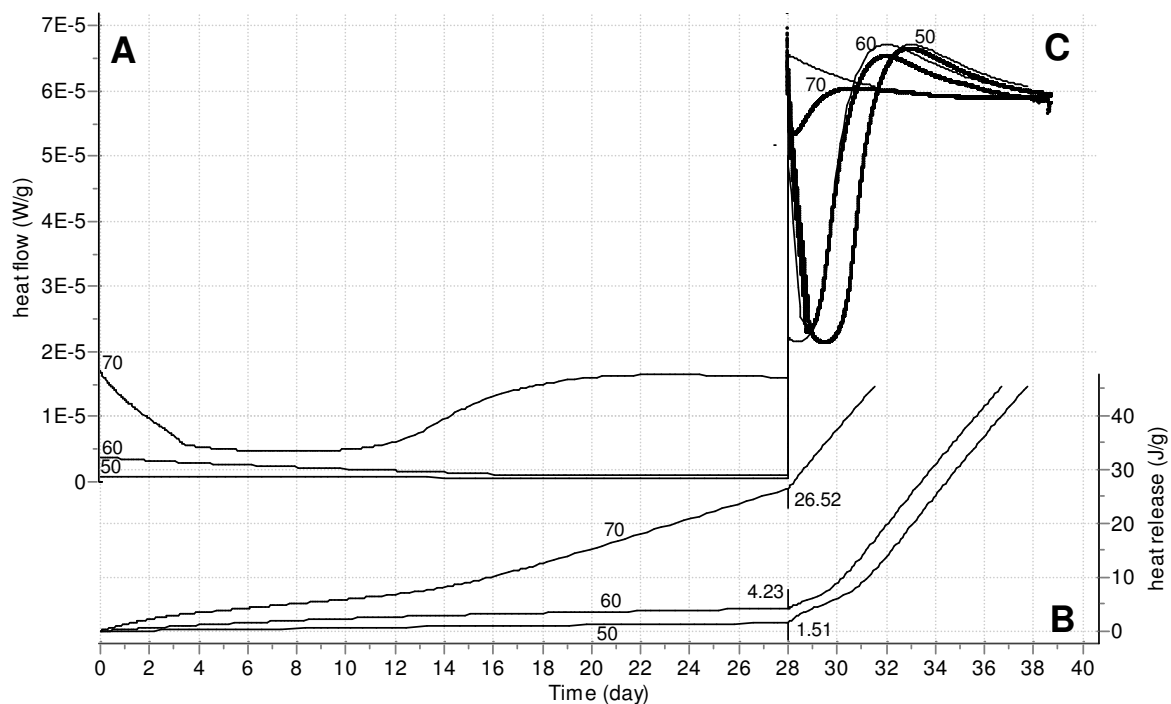
Fig.4 Simulation of the heat flow signals (A) and cumulative heat release (B) for the samples aged during 4 weeks at 50, 60 and 70°C and exposed to 80°C for 10 days. (C) Comparison of the simulated and experimental heat flow traces at 80°C. The aging temperatures and the values of the released heat are marked on the curves in °C and J/g, respectively.

Presented results indicate that having the kinetic parameters of the propellant decomposition one can simulate the heat flow signals at any temperature (here at 80°C) not only for the fresh, but also for the already aged samples, despite the fact that certain, unknown amount of heat was already evolved during aging. This simulation is possible even if the aging process has occurred at any temperature mode, not only isothermally as in the present study.

Such a simulation for the arbitrarily aged sample requires only one experiment performed at 80°C. Due to the fact that the unknown reaction progress, combined with the evolution of certain amount of heat, has already taken place the recorded heat flow signal will be shifted up to lower times as shown in Figs. 1 and 2. Using the kinetic parameters the simulated signal will be numerically adjusted in order to match the experimental curve. This fit will result in evaluation of the amount of heat already evolved during aging. Only for one, certain amount of the heat already evolved before beginning of the experiment at 80°C the experimental curve of the aged sample at 80°C can be correctly matched.

If the sample with the unknown aging history has the same cumulative heat release signal as those aged in controlled way at 60°C for 4 weeks then the amount of the heat released during aging amounts also to 4.23 J/g (see the data presented in Fig. 4B). In turn, if the amount of the heat lost during aging required for the matching of simulated and experimental results at 80°C amounts to 3.2 J/g, this indicates that sample before HFC experiment at 80°C was aged for 12 weeks at 50°C (see data in Tab.1). Of course, such amount of the heat can be evolved under any aging conditions therefore

knowing e.g. the daily temperature fluctuations at any arbitrarily chosen place one can evaluate the duration of the aging which will result in the same heat release. Taking as an example the temperature fluctuations in Las Vegas it is possible to calculate that 3.2 J/g will be released during 11.5 years. The simulation of the heat flow and cumulative heat release for the meteorological profile of Las Vegas is presented in Fig. 5.
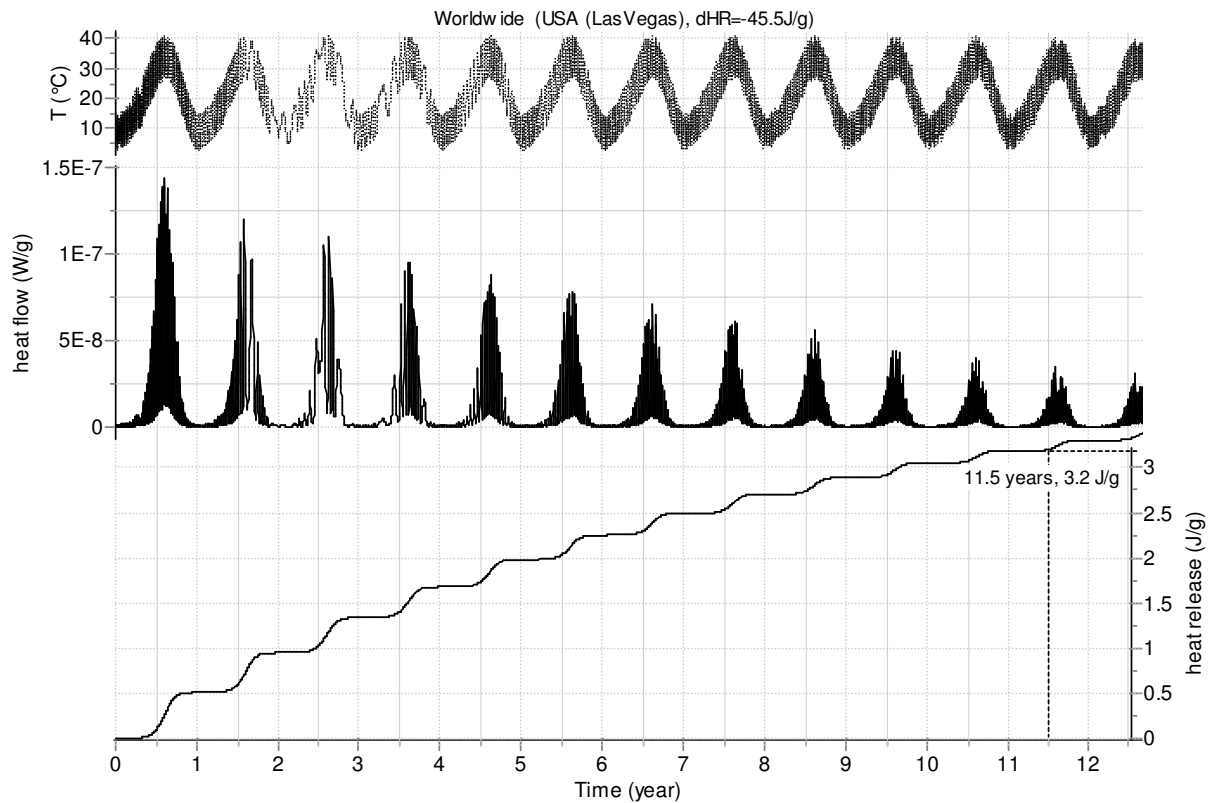

Fig.5 Prediction of the heat flow (reaction rate) and cumulative heat release (progress of the decomposition) for a double base propellant for small calibre applications for the meteorological temperature profiles of Las Vegas. The time required to reach a heat release of 3.2 J/g amounts to ca. 11.5 years. The same heat release is reached if the sample is aged 12 weeks at 50°C (Tab.1).

6. Determination of the service lifetime of the propellants

The studies concerning the evaluation of the service life-time of the propellants based on the measuring e.g. bullets velocity [3] have shown that the materials preserve their required properties till the point when the amount of the released heat due to the exothermic decomposition does not exceed the value of ca. 40 J/g. This amount of the heat is evolved when the decomposition degree lies in the range of the ca. 0.01-0.02. The method proposed in this study allows calculating the time at which, at any applied temperature profile, the heat evolved from the sample will not exceed this value. To illustrate the influence of various temperatures and its fluctuations on the time required for reaching cumulated heat release of 40 J/g, the simulations of the reaction progress were carried out for:
- the temperatures in the range of 25 to 130°C,
- the average daily minimal and maximal temperatures recorded for each day of the year in high temperature climatic categories such Las Vegas USA,

-   the high temperature climatic category A1 according to the STANAG 2895 [13]. This document describes the principal climatic factors which constitute the distinctive climatic environments found throughout the world.

By the extension the heat release can also be calculated similarly for storage temperature profile corresponding to various temperature scenarios and cycles collected by data logger [12].

The results of these calculations are presented in the Table 2 which additionally contains the experimental data collected for the spherical double base propellant [12]. The results once more confirm (see also Tab.1) the higher thermal stability of the sample investigated in the present study: the service life-time i.e. the time in which the amount of the heat evolved from the sample will reach the value of 40 J/g amounts to 1.63 and 2.48 years for the spherical double base propellant and double base powder for small calibre applications investigated in this study, respectively.

When the temperature fluctuations are such as those in Las Vegas, the time to reach a heat release of 40 J/g is around 119.6 years. The storage conditions as fixed in STANAG 2895 [13] for A1 cycles ("extreme hot climate") with daily temperatures fluctuations between 32 and 71°C can be considered as "worst case" in ageing of the propellant. Under these conditions the service lifetime of the propellant amounts to about 160.4 days.

Table 2. Dependence of the time required for the evolution of the 40 J/g due to the decomposition of the propellant on the temperature. The experimental data for another propellant taken from [12] are marked in bold.

T (°C)	Time required for release of 40 J/g		T (°C)	Time required for release of 40 J/g
25	241 years		80	8.97 days (exp and cal) **(7.99 days)**
30	90.6 years		85	4.5 days
35	35.2 years		90	2.29 days
40	14.1 years		95	28.57 hours
45	5.83 years		100	15.16 hours
50	2.48 years	**(1.63 year)**	105	8.16 hours
55	1.08 year		110	4.46 hours
60	5.81 months	**(4.16 months)**	115	149.3 min
65	2.66 months		120	84.3 min
70	38.09 days	**(30.71 days)**	125	48.35 min
75	18.29 days		130	28.07 min

Temperature profiles	Time to 40 J/g
USA, Las Vegas climate conditions	119.6 years
STANAG 2895 A1 cycles ("extreme hot climate", daily 32 and 71°C)	160.4 days

The results of the calculations of the service life-time of the sample exposed to the complicated temperature profiles i.e. to the climate conditions of Las Vegas and those of A1 cycle of STANAG 2895 are depicted in Figs. 6 and 7, respectively.
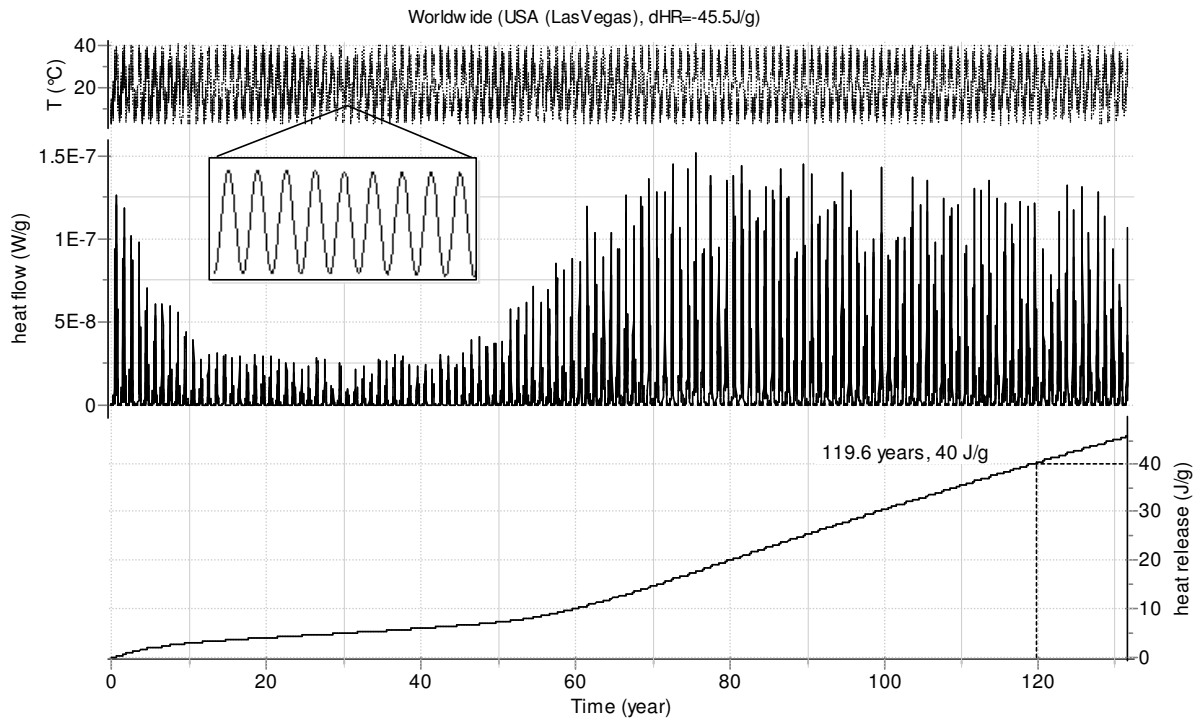
Fig.6 Prediction of the time required for the evolution of the 40 J/g from the double base propellant at the meteorological temperature profiles of Las Vegas.
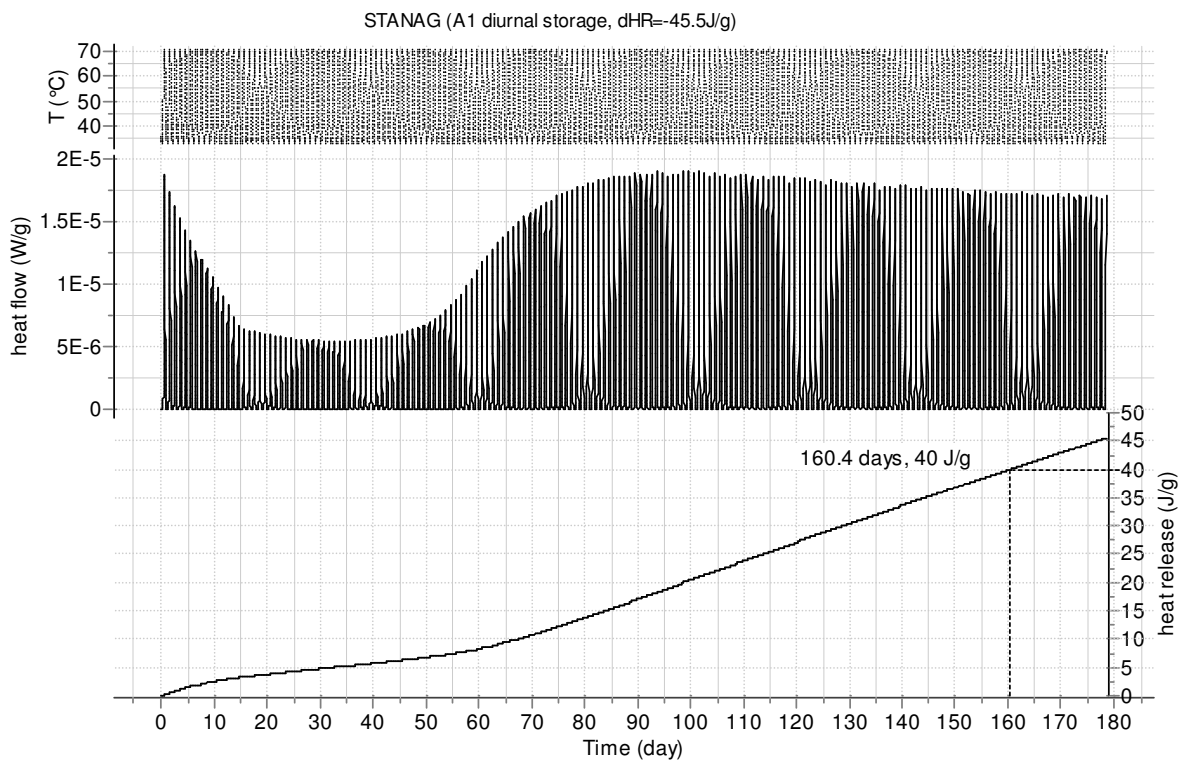

Fig.7 Prediction of the time required for the evolution of the 40 J/g from the double base propellant for the diurnal storage temperature for climatic category A1 according to STANAG 2895.

7. Conclusion

The paper describes the procedure of the simulation of the minor heat release occurring during aging of the energetic materials. The method is based on the determination of kinetic parameters of the decomposition of double base propellant for small calibre applications from the HFC traces. The comparison of the heat flow signals recorded at the same temperature (80°C) for the fresh and differently aged samples shows the significant shift of the signals into the shorter times resulting from the evolution of the certain amount of the heat during aging. The numerical approximation of the shape and shift of the aged samples and referring it to the traces of the fresh sample allowed determination of the kinetic parameters of the reaction by the differential isoconversional method using the principle of the compensation effect. The kinetic parameters were determined for early stage of the decomposition being in the range of 0.01-0.02 of the total decomposition progress.

The knowledge of the kinetics of the propellant decomposition allowed to simulate the reaction progress of the sample under different temperature modes what, in turn, allowed simulating the amount of the heat released from the samples during aging. It was possible to simulate the time at which the total amount of the evolved heat will not exceed the value of 40 J/g being reported in the literature as a value below which the propellant properties remain unchanged. The simulations of the cumulative heat release were carried out for isothermal conditions, the real meteorological temperature profiles and profiles defined according to the STANAG 2895.

The good fit of the experimental data by the simulated curves confirms the validity of proposed method.

References

[1]   B. Roduit, P. Folly, B. Berger, J. Mathieu, A. Sarbach, H. Andres, M. Ramin and B. Vogelsanger, J. Therm. Anal. Cal., 93 (2008) 1, 153–161.
[2]   B. Roduit, W. Dermaut, A. Lunghi, P. Folly, B. Berger and A. Sarbach, J. Therm. Anal. Cal., Vol. 93 (2008) 1, 163–173.
[3]   U. Ticmanis, P. Guillaume, A. Fantin, G. Pantel, J-P. Marchandise, S. Wilker, 3rd Int. Symp. on HFC and its applications for energetic materials, (2002).
[4]   B. Roduit, L. Xia, P. Folly, B. Berger, J. Mathieu, A. Sarbach, H. Andres, M. Ramin, B. Vogelsanger, D. Spitzer, H. Moulard and D. Dilhan, J. Therm. Anal. Cal., Vol. 93 (2008) 1, 143–152.
[5]   AKTS-Thermokinetics Version 3.10 May 2009, Advanced Kinetics and Technology Solutions, http://www.akts.com (AKTS-Thermokinetics software and AKTS-Thermal Safety software).
[6]   A.K. Galwey and M.E Brown, Thermochim. Acta, 300 (1997) 107-115
[7]   M.E Brown and A.K. Galwey, Thermochim. Acta, 387 (2002) 173-183
[8]   W.P.C. de Klerk, L.H. van Broeckhuijsen and P.J. van Ekeren, Proc. 6th Int. Symp. HFC on Energetic Materials, Fraunhofer ICT, Pfinztal-Berghausen, Germany, May (2008) 189.
[9]   Daniel S. Ellison and Anton Chin, Proc. 6th Int. Symp. HFC on Energetic Materials, Fraunhofer ICT, Pfinztal-Berghausen, Germany, May (2008) 303.
[10] U.Ticmanis, P. Guillaume, S. Wilker, G. Pantel, A. Fantin, M. Koch and L. Jeunieau, Proc. 6th Int. Symp. HFC on Energetic Materials, Fraunhofer ICT, Pfinztal-Berghausen, Germany, May (2008) 315.
[11] H. L. Friedman, J. Polym. Sci, Part C, Polymer Symposium (6PC), 183 (1964).

[12] B. Roduit, P. Guillaume, S. Wilker, P. Folly, A. Sarbach, B.Berger, J. Mathieu, M.Ramin and B. Vogelsanger, Proc. 6th Int. Symp. HFC on Energetic Materials, Fraunhofer ICT, Pfinztal-Berghausen, Germany, May (2008) 67.

[13] STANAG 2895 (1990), Extreme climatic conditions and derived conditions for use in defining design/test criteria for NATO forces material, http://www.nato.int/docu/stanag/2895/2895.pdf .