Thermal loading of explosives—Finite difference method with time step reduction

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ABSTRACT

The method of simulation of heat transfer during thermal loading of energetic materials is introduced. The combination of the simple finite difference method with a time step reduction enables the quick and precise calculation of ignition times. The results are in accordance with published model data. The method was also used to simulate heat transfer during the slow cookoff test and the result agrees very well with experimental data.

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1. Introduction

Self-heating and the possibility of the subsequent spontaneous ignition is a very important problem in the field of explosives safety. The thermal decomposition of an energetic material is an exothermic reaction. If the heat generated by the decomposition of the explosive is not conducted away to the surroundings, it will accumulate in the reacting material and increase its temperature. As the decomposition reaction rate increases, more heat is generated. This process can potentially lead to the spontaneous ignition of the material and to thermal explosion.

Thermal explosion theory is based on the comparing of the heat generated by the decomposition reaction with the heat losses into the surroundings. The first thermal explosion theory was suggested by Semenov in 1928 [1] and was based on uniform temperature distribution in the reactant. The second classic theory, proposed by Frank-Kamenetskii in 1939 [2], takes into the account heat conduction in the reactant. If the decomposition reaction obeys Arrhenius kinetics, the heat transfer can be described (according to Frank-Kamenetskii theory) by the following equation:

$$\rho c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \rho Q f(\alpha) A \exp\left(\frac{-E}{RT}\right), \qquad (1)$$

where ρ is density [kg m^{-3}], c is specific heat capacity [J kg^{-1} K^{-1}], T is temperature [K], t is time [s], λ is thermal conductivity coefficient [W m^{-1} K^{-1}], Q is decomposition heat [J kg^{-1}], $f(\alpha)$ is reaction model depending on the conversion α (both α and $f(\alpha)$ are dimensionless), A is pre-exponential factor [s^{-1}], E is activation energy [J mol^{-1}] and R is universal gas constant [J mol^{-1} K^{-1}]. This equation cannot be solved analytically, because of the exponential dependency of the generated heat (the second term on the right side) on temperature. The general reaction model $f(\alpha)$ also makes the solution more difficult. Frank-Kamenetskii solved a simplified form[1] of this equation.

Zinn and Mader [3] solved the Eq. (1) using the zero order reaction model in 1960. They combined analytical solution of unsteady heat transfer for infinite slab, infinite cylinder and sphere (Eq. (1) without the second term on the right side) with the time discretization. The time discretization enabled evaluation of the temperature increase by the chemical reaction (the second term on the right side of Eq. (1)). The extension of their solution including the first order reactions is described two years later by Zinn and Rogers [4].

Eq. (1) was successfully solved by Sućeska [5] using the finite difference method and a zero order kinetic model, as implemented in his THERMEX code. Sućeska and Matečić-Mušanić improved the THERMEX program to include arbitrary reaction order and an autocatalytic reaction model two years later [6]. Another solution of Eq. (1) was proposed by Aydemir et al. [7]. Their code REACON-1D uses the finite element method and a zero order kinetic model. The use of finite element method for the solution of the Eq. (1) in the AKTS thermal safety software has been reported by Roduit [8].

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[1] He used one dimensional geometric shapes, a zero order reaction model ($f(\alpha) = 1$), simplification of the exponential term, and constant temperature as the boundary condition.
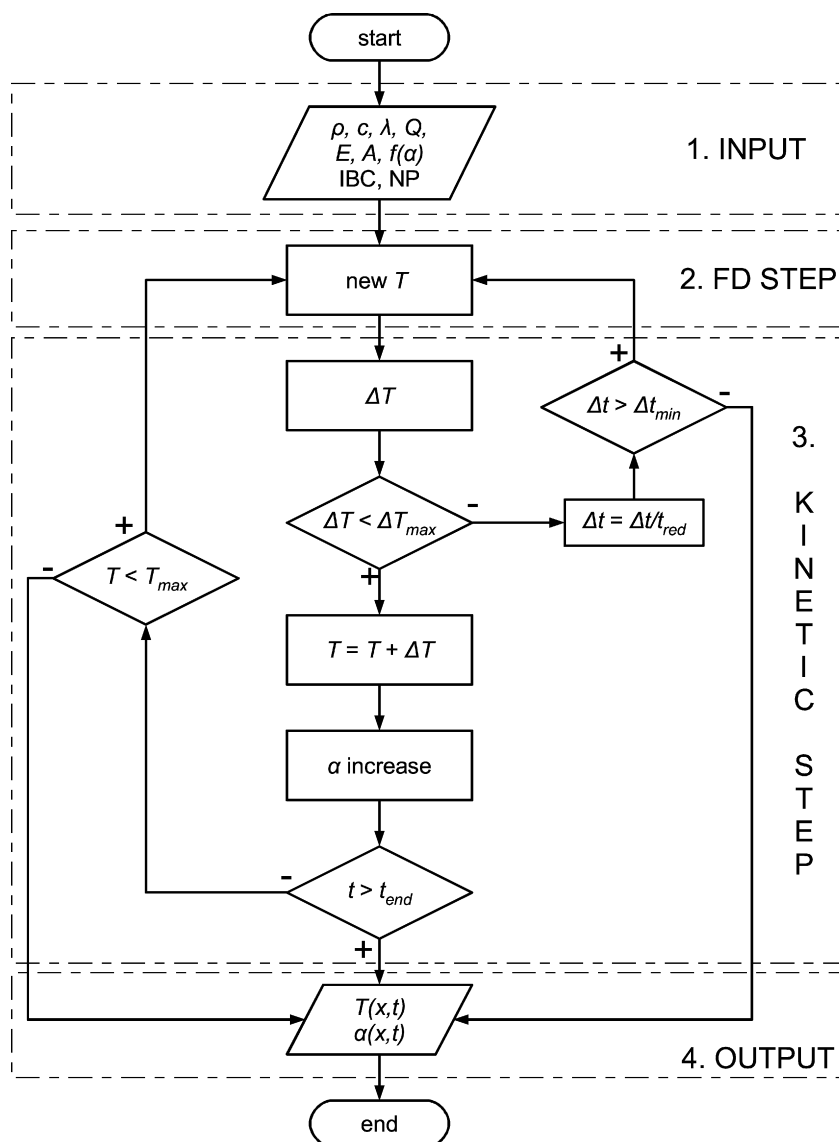
Fig. 1. The flowchart scheme of the calculation (IBC—initial and boundary conditions, NP—numerical input parameters, FD—finite difference).

The self-ignition was also modeled as a part of slow cookoff simulation by other labs using their in house codes (SNL (USA) [9,10], LLNL (USA) [11–13]). The cookoff was also successfully simulated in TNO (Netherlands) [14] and in DSTO (Australia) [15] using modifications of existing finite element codes.

The purpose of this article is to introduce a simple solution of Eq. (1). The presented solution was derived from the finite difference method applied by Sućeska [5,6] which is modified using a time step reduction. A time step reduction ensures the precision of the results and the speed of their calculation.

2. Calculation

The Eq. (1) was solved using the finite difference method with the time step reduction. The procedure of calculation can be divided into four parts, as displayed in Fig. 1. The first part is the input of the data (material properties, initial and boundary conditions ('IBC' in Fig. 1), numerical parameters ('NP' in Fig. 1). The second and the third part are the calculation steps. The second part is the standard heat transfer calculated by explicit finite differences ('FD step' in Fig. 1, explained in Section 2.2). The third part is the kinetic calculation of heat evolved from the decomposing material ('Kinetic

step' in Fig. 1, explained in Section 2.3). This third part influences the changes of the time step. The second and the third parts are repeated until the simulation is ended. The last part is the output of the data.

2.1. Input parameters

Three kinds of input parameters are needed for the calculation. The physical properties[2] (ρ, c and λ) and the description of the decomposition reaction (Q, E, A and $f(\alpha)$) are needed to describe the simulated material.

The initial and boundary conditions ('IBC' in Fig. 1) are to be specified also. The distribution of temperature and degree of conversion for the starting time of the simulation and the description of the boundary temperature (constant or time dependent, direct

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[2] The physical properties are dependent on temperature. It is suitable to use their values for temperatures close to the temperatures used in the simulation. E.g. if the slow cookoff is modeled with the starting temperature 90 °C and the ignition temperature 140 °C, the values of ρ, c and λ should be determined cca at 120 °C. In the small temperature interval they can be considered constant.
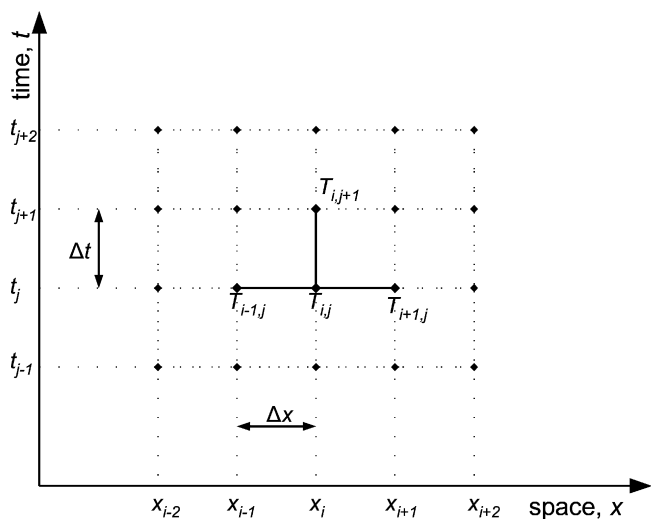
Fig. 2. The solution grid from the finite difference method and the explicit finite difference stencil.

or convection) fall into this category. The boundary conditions are described in Appendix A.

The third kind of parameters are the parameters influencing the numerical solution ('NP' in Fig. 1). It is necessary to divide the modeled body into the equally spaced nodes and to specify the distance between nodes (Δx). The initial time step is calculated automatically from the stability condition (see Section 2.2). The time step is monitored and reduced during the calculation. To control the time step reduction, two other parameters are needed. The maximum temperature rise (ΔT_{max}) during one time step due to the decomposition of the energetic material, and the reduction factor for the decrease of the time step (t_{red}). The time step control is described in the Section 2.3 below. To indicate ignition, the maximum allowable temperature T_{max} and the minimum allowable time step Δt_{min} are used. The last parameter is the end time, at which the simulation is stopped, if the ignition does not occur.

2.2. Finite difference step

The principle of finite difference methods[3] is to approximate the derivatives by differences and to solve the resulting algebraic equations. The solution is obtained in discrete points (nodes) and in discrete time intervals. The discretization (for the 1D example) and the resulting solution grid is displayed in Fig. 2. The points represent the temperatures, the i and j subscripts correspond to space and time discretization. In case of 1D bodies the space coordinate x corresponds to the distance from the center of the symmetry (the central plane of an infinite slab, the axis of an infinite cylinder and the center of a sphere).

The explicit scheme stencil is also indicated in Fig. 2. The word explicit means, that every new value of temperature $T_{i,j+1}$ is calculated from the results obtained in the preceding time step ($T_{i-1,j}$, $T_{i,j}$ and $T_{i+1,j}$):

$$T_{i,j+1} = T_{i,j} + \frac{\lambda \Delta t}{c\rho}\left(\frac{T_{i+1,j} + T_{i-1,j} - 2T_{i,j}}{(\Delta x)^2} + \frac{a}{x}\frac{T_{i+1,j} - T_{i,j}}{\Delta x}\right), \quad (2)$$

where x is space coordinate (the distance from the mid plane, axis or center for the case of infinite slab, infinite cylinder and sphere, respectively) and a is the shape factor.[4]

The explicit scheme is very simple to use. However, this simplicity is balanced by the stability of this method [16]. The explicit method stability is conditioned by ratio of the space and time steps. In case of the heat conduction, the method is stable if the following stability condition is fulfilled:

$$\frac{\lambda \Delta t}{\rho c (\Delta x)^2} \leq \frac{1}{2} \quad (3)$$

The initial time step is calculated using the maximum Δt allowed by the condition (3). During the calculation, the time step can be reduced, if it is necessary as described below.

2.3. Kinetic step

The temperatures from the finite difference step are the temperatures obtained from heat transfer without any chemical reaction. During thermal loading of explosives heat is also produced by the decomposing material. The corresponding temperature rise $\Delta T_{i,j+1}$ is calculated from the following equation:

$$\Delta T_{i,j+1} = \frac{\Delta t}{c}Qf(\alpha_{i,j})A\exp\left(\frac{-E}{RT_{i,j+1}}\right) \quad (4)$$

where $T_{i,j+1}$ are nodal temperatures from the finite difference step and $\alpha_{i,j}$ are nodal values of conversion.

The conversion α is monitored separately in each node. If the reaction heat Q is known, the amount of heat produced from decomposition during the time step divided by Q is directly proportional to the increase of the conversion. The reaction model $f(\alpha)$ can be specified in an arbitrary form. The usual models (such as first order, power law, autocatalytic model) can be used. It is also possible to express the reaction model in the tabular form. In this case the values of $f(\alpha)$ are calculated by linear interpolation. This approach is sometimes useful to simulate some complex decomposition processes.

2.3.1. Time step reduction

The stability condition (3) ensures the stability of the finite difference solution. However this condition does not ensure sufficient precision of the results for the simulation of the thermal loading of explosives. The solution is precise if the decomposition of the explosives is slow, i.e. the amount of self-heat produced is small. If the explosive produces a lot of heat, the maximum time step is too big and the resulting solution is inaccurate. In this case, precision can be improved by using the smaller time steps for the whole simulation (e.g. Sućeska and Matečić-Mušanić [6] state that the stability condition $\lambda \Delta t/\rho c(\Delta x)^2$ should be smaller than 0.01). This approach gives precise results, but the calculation takes too long time. A quick and accurate solution can be obtained by using the time step reduction.

The principle of the time step reduction is based on the amount of heat evolved by the decomposing explosive. If the amount of produced heat is low, the calculation is carried out with the biggest possible time step, fulfilling the stability condition (3). As soon as the decomposing explosive produces more heat, the solution becomes less accurate despite the fact that it is still stable. To sustain the precision, the last results $T_{i,j+1}$, $\Delta T_{i,j+1}$ have to be canceled and their calculation is repeated with the smaller Δt. The temperature increment $\Delta T_{i,j+1}$ caused by the explosive decomposition can

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[3] The finite difference method itself is described in any general textbook of numerical mathematics, e.g. [16], and therefore only a brief description follows.

[4] The shape factor a originates from the transformation of the Laplace operator ∇^2 into the symmetric one dimensional geometry ($a = 0$ for the infinite slab, $a = 1$ for the infinite cylinder and $a = 2$ for the sphere).

be used as a measure of heat production. If the maximum $\Delta T_{i,j+1}$ is higher that limit value (e.g. $\Delta T_{max} = 1\,°C$), the time step is reduced by t_{red} (e.g. $t_{red} = 3$).

The parameter ΔT_{max} plays a crucial role in the time step reduction. Its value should be sufficiently low to achieve enough precise results. In case of using a high ΔT_{max} value, a large amount of heat can be evolved during one time step, the time behavior of temperature and conversion will not be smooth and the results will not be accurate. Values of ΔT_{max} larger than $3\,°C$ usually cause these inaccuracies. The second parameter t_{red} is less important. Small values of t_{red} close to one increase the number of reductions. Large values of t_{red} cause rapid decrease of the time step during a single reduction and prolongate the calculation.

2.4. Output parameters

The calculation ends by reaching of the end time t_{end}, or by the ignition of the material. Two ways to identify the ignition are possible. The first one is to specify the maximum allowable temperature T_{max}. If the material reaches this temperature (reasonable value is e.g. $T_{max} = 500\,°C$), ignition is assumed and the calculation ends. The second way is to specify the rate of temperature rise inside the material. This can be done through the minimum allowable time step Δt_{min}. If the time step is reduced to this minimum value, the temperature rise is so big, that ignition can be assumed.[5] The t_{end} and T_{max} are tested during every time step, the Δt_{min} is tested after each time step reduction, as can be seen in Fig. 1.

The output parameters are dependencies of temperature $T(x, t)$ and conversion $\alpha(x, t)$ in discretized space and time. From these dependencies the time and the place of ignition can be expressed. In the case of a time dependent boundary, the temperature of the boundary at the time of ignition can be calculated.

2.5. Method validation

The whole algorithm was implemented using the GNU/Octave programming language. GNU/Octave is an open source software intended for numerical computation and downloadable from the web pages [17]. The inputs and outputs are in the form of text files.

As a test of the method suitability, the results were compared with previously published modeled data for RDX (Sućeska and Matečić-Mušanić [6] and Aydemir et al. [7]). The slow cookoff test of Semtex 1A was also simulated by this method, to get a comparison with real experimental data. The properties of both materials are summarized in Table 1.

2.6. Model example

The results for the model simulation of an RDX sphere subjected to isothermal boundary conditions have been published [6,7]. The diameter of the sphere was 25.4 mm, the initial temperature was $25\,°C$ and the temperature of the surroundings was between 180 and $260\,°C$. The properties of RDX are stated in Table 1. The simulation was carried out in the spherical coordinates for the surrounding temperatures 180, 200, 220, 240 and $260\,°C$. The conditions (geometry, initial and surrounding temperature, material properties) were the same as were used in references [6,7].

Table 1
Properties of the explosives, used for the simulation.

	RDX [6]	Semtex 1A [18]
ρ [kg m^{-3}]	1800	1493.6
λ [W m^{-1} K^{-1}]	0.293	0.1531
c [J kg^{-1} K^{-1}]	2093	1480.9
E [J mol^{-1}]	1.99×10^5	2.002×10^5
A [s^{-1}]	3.16×10^{18}	1.091×10^{20}
$f(\alpha)$ [−]	1	$(1 - \alpha)$ [a]
Q [J kg^{-1} K^{-1}]	2.093×10^6	$4.024\,1 \times 10^6$
Numerical parameters [b]		
Δx [m]	6.35×10^{-5}	7×10^{-4}
ΔT_{max} [°C]	1	1
t_{red} [−]	3	3
T_{max} [°C]	500	500
Δt_{min} [s]	1×10^{-4}	1×10^{-4}
t_{end} [s]	2000	65 000

The properties of RDX are taken from literature [3]. These parameters are the same as used for the simulation in [6,7]. The determination of Semtex 1A properties is described in [18].

[a] The zero order reaction model was used in [18], the first order reaction model is used in this work.

[b] This work.

Table 2
Times to ignition for RDX spheres.

T_s [°C]	Time to ignition [s]		
	THERMEX [6]	REACON-1D [7]	This work
180	1051.8	1056.09	1049
200	466.9	467.88	466
220	166.1	167.08	166
240	44.0	44.42	45.0
260	10.3	10.59	10.8

2.7. Experimental comparison

The slow cookoff test[6] of Semtex 1A was also modeled using the finite difference approach with the time step reduction. Semtex 1A is a Czech commercial plastic bonded explosive. The determination of its properties, slow cookoff test and the simulation of heat transfer during cookoff using LS-DYNA code is described in [18].

The cylindrical charge had a diameter of 21 mm and a length of 90 mm. The initial temperature of the charge was $90\,°C$ and the heating rate was $3.3\,°C$/h. A convection boundary was used with the heat transfer coefficient $h = 100\,W\,m^{-2}\,K^{-1}$, the surroundings in this case is the air, which heats the charge.[7] The simulation was carried out in cylindrical coordinates, the shape was considered as an infinite cylinder.

3. Results and discussion

The results of the simulations for the RDX model data is stated in Table 2. The simulations were ended by decreasing the time step below the minimum value $\Delta t_{min} = 10^{-4}$ s in all cases. The Table 2 also shows the comparison of achieved results with the already published results of the similar simulations (same material properties, same geometry, same initial and boundary conditions).

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[5] In case of $\Delta T_{max} = 1\,°C$ and $\Delta t_{min} = 10^{-4}$ s, the corresponding heating rate is $10^4\,°C$/s.

[6] The slow cookoff test is a method for the evaluation of thermal stability of explosives. The explosive charge is placed in the cylindrical steel case and heated slowly ($3.3\,°C$/h) to decomposition. In this case the heating was realised by fanning with a hot air. The temperature of the surroundings at the time of ignition is one of the monitored parameters.

[7] The charge without the confinement was simulated in this case. The convection boundary enables heat to be transferred into the surroundings in the case that the temperature of the surface of the charge is higher than the temperature of the surrounding air.
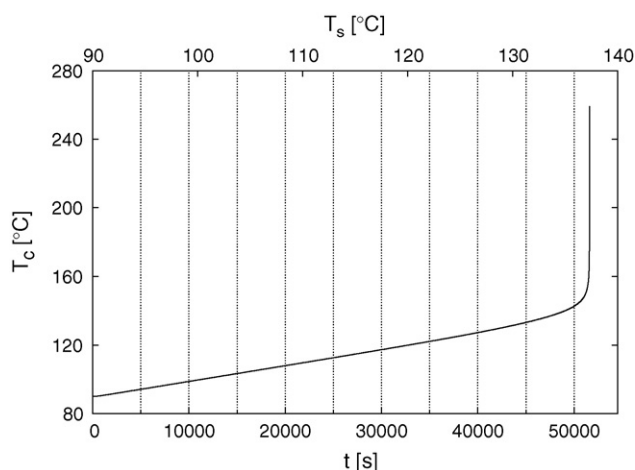
Fig. 3. Temperature behavior in the center of the charge during the simulation of slow cookoff test of Semtex 1A. The upper ordinate corresponds to the surrounding air temperature.

Table 3
Ignition temperatures for the slow cookoff test of Semtex 1A.

	Ignition temperature [°C]
Experimental [18]	136.9 ± 2.2
LS-DYNA simulation [18]	138.0
This work	137.3

The THERMEX code [6] uses finite difference method without time reduction, and the REACON-1D [7] code uses finite element method. The differences between published results and the results presented in this work are small. This comparison shows, that presented algorithm gives results similar to the other comparable codes.

The simulation of the Semtex 1A slow cookoff test was also ended when the time step was reduced to 10^{-4} s. The modeled temperature rise in the center of the charge is displayed in Fig. 3. The ignition was predicted to occur in the center of the charge at time 51 605 s and corresponding temperature of the surrounding air was 137.3 °C (calculated from the boundary condition $T_s[°C] = 90 + 9.1667 \times 10^{-4}t$ [s]). The experimental value was 136.9 °C[8] and the surface temperature for the ignition from the LS-DYNA code [18] is 138.0 °C.[9] All discussed ignition temperatures are stated in Table 3.

The reduction of the time step for the case of the simulation of Semtex 1A slow cookoff test is illustrated in Fig. 4. The maximum value of the time step (in accordance to the stability condition (3)) is used up to time 51 565 s. At this time, the production of self-heat from the sample becomes greater as can be seen from the $\max(\Delta T_{i,j+1})$ curve. The temperature rise will be bigger than 1 °C in the next time step, if the Δt is not reduced. After the reduction, the maximum temperature rise falls down and gradually grows. Again, if an overrun of the $\Delta T_{\max}$ occurs, another time step reduction takes

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[8] The slow cookoff test was carried out three times, the temperatures were measured in the surrounding air, on the confinement and in the center of the sample. The value 136.9 °C is the mean from all nine measured temperatures. The standard deviation was 2.2 °C [18].

[9] The simulation of heat transfer during cookoff in [18] was carried out in the LS-DYNA commercial code. This code is intended for the simulation of fast dynamic processes primarily and is not able to calculate the kinetics of chemical reactions. Therefore the only applicable kinetic model is the zero order reaction ($f(\alpha) = 1$ in Eq. (1)). Despite this fact, the ignition temperature obtained from the LS-DYNA code was very similar to the experimental data.
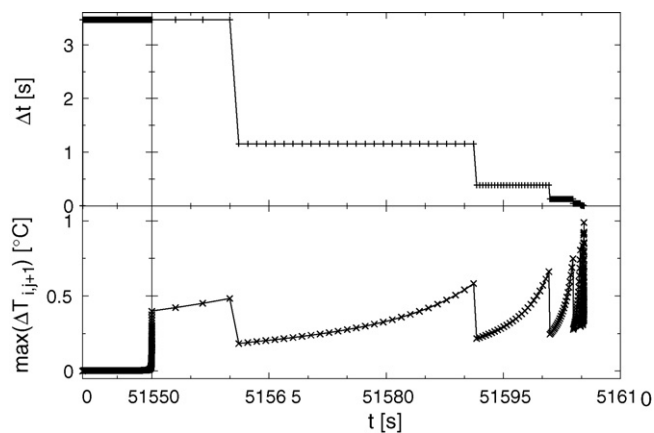

Fig. 4. The gradual reduction of the time step Δt and the maximum temperature rise during the time step $\max(\Delta T_{i,j+1})$ in the case of the simulation of the slow cookoff test of Semtex 1A.

place. This process is repeated until the minimum time step $\Delta t_{\min}$, the maximum temperature $T_{\max}$ or the end time t_{end} is reached.

The gradual reduction of the time step takes place only during last 40 s of calculation in this example. Until this time, the maximum time step fulfilling the stability condition (3) can be used. Using the maximum time step as long as possible improves the speed of the calculation. Subsequent use of the time step reduction ensures good precision as the heat production grows.

4. Conclusion

The introduced method for the simulation of heat transfer in thermally loaded explosives is simple to use and the results are in agreement with published model examples (RDX sphere) and also with experimental data (Semtex 1A slow cookoff test). The simulation is very fast due to the time step reduction and sufficient precision is also ensured. The independent calculation of conversion α enables the usage of arbitrary reaction models, which is another advantage of this approach.

Acknowledgment

Appendix A. Boundary conditions

It is necessary to specify the initial and boundary conditions to solve the Eq. (1) by finite difference method. The initial conditions are the temperatures and conversions in each node in the time when the calculation starts. The boundary condition describes the temperature of the surface of the modeled body. The surface temperature T_s can be specified directly as a function of time in the simplest case. This approach has a disadvantage in case of self heating. E.g. consider the simplest case with the constant surface temperature. If the temperature of the sample starts to rise up to temperature of the surroundings, the temperature of the surface node is still maintained at constant value. Therefore any heat cannot be transferred from the explosive into the surroundings.

The other common method is to specify the temperature of a surrounding media (usually fluid, but it can be e.g. a steel container). In this case it is necessary to specify a convection heat transfer coefficient h [W m^{-2} K^{-1}]. The surface temperature T_s is calculated

from:

$$h(T_s - T_f) = -\lambda \frac{T_s - T_k}{\Delta x}, \tag{A.1}$$

where T_f is the fluid temperature and T_k is the temperature in the node neighboring to the surface. In this latter case, heat can be transferred in both directions between the modeled body and the surrounding fluid. The direction of heat transfer is depended on the difference of the temperatures $T_s - T_f$. The fluid temperature T_f can also vary in time, e.g. in case of the linear heating rate.

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