On the Critical Detonation Diameter of Nitromethane Sensitized by Glass Microballoons

Ermolaev B.S.[(1)], **Khasainov B.A.**[(1)]
Presles H.-N. and Vidal P.[(2)]

(1) Institute of Chemical Physics, RAN, 117334, Moscow, RUSSIA
(2) Laboratoire de Combustion et de Detonique, UPR 9028 CNRS, ENSMA, 86960 Futuroscope cedex (Poitiers), France

The effect of high explosive sensitization by means of heterogeneous inclusions is widely known and used in many applications. For example, glass microballoons (GMB) are used to sensitize emulsion explosives. GMB are also used to study the effect of heterogeneity size and concentration on detonation performance of gelled nitromethane-GMB mixtures [1,2]. The main advantage of such heterogeneous explosives is that their microstructure is much more precisely controlled than that of porous solid explosives. We thus are conducting a detailed program of investigations of detonation performance and shock sensitivity on model nitromethane-GMB mixtures, hoping that this approach will shed light on detonation reaction mechanism in heterogeneous explosives.

Here, we first describe a model of detonation reaction zone in heterogeneous GMB-sensitized explosives based on the assumption that the heat release rate can be represented as the product of normal burning (or regression) rate and specific surface of burning fronts diverging from the GMB surface. The origin and evolution of these burning fronts is described, taking into account the process of GMB deformation, dynamics of the glass and nitromethane heating due to viscous dissipation and heat conduction in and around the GMBs [3]. We then use our model to calculate the charge diameter effect and the critical detonation diameter in GMB sensitized liquid explosives according to the Detonation Shock Dynamics theory [4,5]. We finally compare our numerical results with the experimental data for nitromethane-GMB mixtures and show that the proposed model of reaction zone can be used for quantitatively predicting the charge diameter and confinement effects on GMB-sensitized explosive detonation.

DESCRIPTION OF THE REACTION ZONE MODEL

We consider a steady axisymmetric detonation wave traveling at a constant velocity D in a cylindrical confined charge of heterogeneous liquid explosive. The explosive is a mixture of nitromethane gelled by a small amount of PMMA and uniformly distributed monosized GMBs. Based on the ZND model [6], the detonation wave is considered as a leading shock wave with a subsequent reaction zone. Due to the charge diameter effect, the detonation front is curved and the detonation performance depends on the confinement parameters. The reaction zone flow is described using the multi-phase flow theory [7]. Three phases are considered: the GMBs (subscript *1*), the gelled nitromethane (2) and the reaction products (3). We make the assumptions that the three phases have the same particle velocity and that the condensed explosive, the GMB glass shell and the reaction products have the same pressure P different from the GMB void pressure P_v. In a shock-fixed reference frame, the governing equations then are :

$$(u_z - D)\frac{\partial \rho_\Sigma}{\partial z} + \rho_\Sigma \frac{\partial u_z}{\partial z} + u_r \frac{\partial \rho_\Sigma}{\partial r} + \rho_\Sigma \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) = 0 \qquad (1)$$

$$\rho_\Sigma (u_z - D)\frac{\partial u_z}{\partial z} + \rho_\Sigma u_r \frac{\partial u_z}{\partial r} + \frac{\partial P_\Sigma}{\partial z} = 0 \qquad (2)$$

$$\rho_\Sigma (u_z - D)\frac{\partial u_r}{\partial z} + \rho_\Sigma u_r \frac{\partial u_r}{\partial r} + \frac{\partial P_\Sigma}{\partial r} = 0 \qquad (3)$$

$$(u_z - D)\frac{\partial(\phi_i \rho_i)}{\partial z} + \phi_i \rho_i \frac{\partial u_z}{\partial z} + u_r \frac{\partial(\phi_i \rho_i)}{\partial r} + \phi_i \rho_i \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r}\right) = I_i \quad ; i=2,3 \qquad (4, 5)$$

$$(u_z - D)\left(\frac{\partial e_i}{\partial z} + P\frac{\partial V_i}{\partial z}\right) + u_r \left(\frac{\partial e_i}{\partial r} + P\frac{\partial V_i}{\partial r}\right) = \varepsilon_i \quad ; i=2,3 \qquad (6, 7)$$

Eqs.(1,2,3) are the continuity equation and the axial and radial components of the momentum equations for the three-phase mixture, Eqs.(4,5) and (6,7) express conservation of mass and energy of nitromethane and reaction products respectively, z is the distance from the shock front along the charge axis, r is the radial coordinate, u_z and u_r are the axial and radial components of particle velocity, ϕ_i, ρ_i, $V_i=1/\rho_i$ and e_i are the volume fraction, the thermodynamic density, the specific volume and the internal energy of each phase (i=1,2,3, the effective GMB density ρ_1 is defined below), I_i and ε_i are the rates of inter-phase mass and energy exchange due to burning, ρ_Σ and P_Σ are the mixture density and pressure:

$$\rho_\Sigma = \sum_{i=1}^{3} \phi_i \rho_i \,, \quad P_\Sigma = \phi_v P_v + (1-\phi_v) P \qquad (8, 9)$$

ϕ_v void volume fraction, $P_v = P_{v0}\,(a_0 / a)^{3\gamma}$ and P_{v0} are the current and initial pressure in the void, a and a_0 are the current and initial void radii, γ is the polytropic index of the gas filling the void. There is a relationship between ϕ_v and the GMB volume fraction ϕ_1 which reads as $\phi_1 = \phi_v\,(g / a)^3$ where g is the external GMB radius. We complement these macro-level equations by studying the GMB deformation behind the shock front in order to find the evolution of GMB radii and ignition time. To this end, we consider the spherical micro-cell [3] which initially consists of three spherical layers : a void inside the GMB, a thin glass shell and a layer of nitromethane adjacent to the GMB. After the reaction ignition, a forth layer of gaseous reaction products is formed between the glass and the nitromethane. This layer is separated from the condensed explosive by an infinitely thin burning front propagating outward from the GMB. Initial radii of the cell are first obtained from the GMB size and concentration in the mixture. Because of the high glass viscosity, the GMB deformation in the shocked explosive then follows a spherically symmetric viscous regime [3]. The energy dissipated during the GMB deformation is predominantly released in the glass layer. A thin layer of nitromethane adjacent to GMB is mainly heated by heat conduction from the glass and, finally, nitromethane is ignited at the glass-nitromethane contact surface. The ignition delay is defined as the time for which the heat release rate due to the chemical reaction becomes «infinitely» fast. After ignition, the chemical reaction proceeds in a surface burning mode, with infinitely thin combustion zone, from the GMB surface through the nitromethane layer. We assume that the burning rate follows an empirical burning law, with pressure and initial temperature dependencies taken into account:

$$U_p = B P^{\upsilon} \exp[\beta_T (T_2 - T_o)] \qquad (10)$$

B, υ and β_T are the burning law parameters estimated from independent experimental data on burning of nitromethane under near-detonation conditions, To=293 K is the reference temperature. Furthermore, the bulk decomposition rate of nitromethane behind the shock front is expressed as the product of the normal regression rate Up and the specific burning surface Sf. Hence, one finds for the rates of mass inter-phase exchange in Eqs.(4-7):

$$I_2 + I_3 = 0\,, \quad \begin{cases} \text{prior to ignition} : I_2 = 0,\ I_3 = 0 \\ \text{after ignition} \quad : I_3 = \rho_2 U_p S_f \end{cases} \qquad (11)$$

We compute S_f by assuming that the spherical hot spots burn in two stages, a progressive one and a digressive one. Simple geometrical considerations show that, during the first stage, the burning front radius $r_f = g\,(1 + \phi_3/\phi_1)^{1/3}$ so that S_f increases at first as r_f^2,ie

$$S_f = 4\pi n_1 g^2 (1 + \phi_3/\phi_1)^{2/3} \qquad (12)$$

$n_1 = \phi_1 / (\frac{4\pi}{3} g^3)$ the GMB number per unit volume of the mixture. Consequently, at the instant of ignition, S_f equals the specific surface of collapsing GMB which differs from the initial specific surface of heterogeneities in the nitromethane-GMB mixture

$A_s = 4\pi g^2_0 n_{10} = 3\phi_{10} / g_0$. Once neighboring burning fronts have coalesced, the burn-out of residuals proceeds with their specific surface digressively dropping to zero at the end of the process :

$$S_f = (S_f)_c [\phi_2 / (\phi_2)_c]^{2/3} \tag{13}$$

$(S_f)_c$ and $(\phi_2)_c$ are the specific burning surface and nitromethane volume fraction at the instant of coalescence of diverging flame fronts which takes place when $(\phi_2)_c = \pi / 6$ For the rate of energy exchange in Eqs.(4-7) one has $\varepsilon_2 = \varepsilon_3$ before ignition and

$$\varepsilon_2 = 0; \quad \varepsilon_3 = (I_3 V_3 / \phi_3)(e_2 + PV_2 - e_3 - PV_3) \tag{14}$$

after ignition The system of governing equations is closed with the normalizing condition:

$$\sum_{i=1}^{3} \phi_i = 1$$

and the equations of state of nitromethane and its reaction products. We used HOM equations of state [8] but modified temperature of nitromethane following reference [9].

APPLICATION OF THE MODEL TO ANALYZE THE CHARGE DIAMETER EFFECT AND CRITICAL DETONATION DIAMETER FOR GMB-SENSITIZED EXPLOSIVES

The calculation of the detonation velocity in a finite-diameter charge requires to take into account the influence of the explosive confinement on the detonation front shape. A fully two-dimensional treatment of this problem is quite complicated and, instead, we used a simpler approach, the so-called Detonation Shock Dynamics (DSD) theory [4,5] This theory leads to the use of quasi-one-dimensional, steady state (Q1DSS) balance equations for describing the reactive flow sustaining the curved shock front, if the thickness of the one dimensional plane detonation reaction zone is much smaller than the shock mean radius of curvature The main result of this theory is that the detonation velocity component Dn normal to the detonation front is a unique function of the shock mean curvature K at any point on the shock front. The $Dn(K)$ relation can be used to obtain the shape of the steady cylindrically symmetric detonation front propagating at a constant velocity D owing to the following set of geometrical identities and boundary conditions [4]

$$D_n = D\sin(\beta) \qquad (\beta \text{ the angle the shock locus makes with the charge axis})$$

$$\frac{d\beta}{dr} = -\frac{K - \cos(\beta)/r}{\sin(\beta)} \qquad \frac{dz}{dr} = \frac{1}{\tan(\beta)} \tag{16}$$

$\beta = 90^o$ at $r=0$ (the charge axis), $\beta = \beta_e$ at $r=r_e = d/2$ (the edge of the charge)

Here, r and z are the radial and longitudinal shock coordinates, K is the known function of D and β is found by reversing the function $Dn(K)$. The second boundary condition at $r=re$ defines a unique value of detonation velocity for a given charge diameter $2r_e$. The angle β_e between the shock locus and the flow axis at the charge edge is defined by solving the interaction problem between the detonation wave and the charge confinement With known value of β_e, one can integrate Eq.(16) with various detonation velocities D thereby defining the $d(D)$ relationship between the charge diameter and the detonation velocity. When the charge diameter is decreased, the detonation velocity decreases and the curvature radius increases due to the enhancement of lateral energy losses In this approach, the existence of a critical detonation diameter is due to the impossibility of detonation propagation when the front curvature exceeds some threshold value This means that the $Dn(K)$ curve must exhibit a particular point with infinite slope According to [5], the calculation of the diameter effect must be based on the upper branch of this curve The latter starts at a value of Dn equal to the CJ plane detonation velocity, which correspond to the zero curvature point and terminates at the particular point with infinite slope, which corresponds to the maximum possible value of front curvature This feature of the $Dn(K)$ relation implies that the resulting dependence $D(d)$ has also a threshold point at some critical value of the charge diameter below which a steady detonation propagation is no longer possible.

Thus, to analyze the charge diameter effect in a GMB-sensitized explosive, one first needs to define the $Dn(K)$ dependence. This can be achieved by noticing that the governing equations along the flow central streamline reduces to the quasi-one dimensional ones because of the following symmetry conditions:

$$u_r = 0; \ \partial u_r / \partial z = 0; \ \lim_{r \to 0}(u_r / r) = (\partial u_r / \partial r)_{axis} \text{ for all } z > 0 \tag{17}$$

The shock curvature K enters the problem owing to the fundamental DSD approximation [4]:

$$(\partial u_r / \partial r)_{axis} = (\partial u_r / \partial r)_{shock} = (D - u_z) / R_a \qquad (18)$$

$R_a = 2/K$ is the shock radius of curvature on the charge axis where $D=Dn$. The $Dn(K)$ is then obtained by means of a shooting method. The Q1DSS equations are integrated for fixed values of D to find the corresponding values of K for which the integral curves goes through a saddle type point (the sonic locus). The shock front flow parameters at z=0 are found from the traditional jump conditions assuming that GMBs are not deformed at the shock front. Finally, to integrate Eq.(16) at a given D, we also need the angle β_e which, generally, depends on the detonation velocity and on the material properties of the confinement and the explosive and also on the nature of the interaction between the detonation front and the confinement (regular refraction, refraction with rarefaction wave, irregular refraction with formation of Mach configuration, unsteady interaction with a shock wave propagating in the confinement ahead of the detonation front). For the explosive under consideration, and due to the wide ranges of initial density and detonation velocity caused by variations of GMB concentration and charge diameter, all the aforementioned regimes of interaction are realized. This is why the problem of correct definition of β_e is very complicated. To simplify the analysis and the data interpretation, we use three typical constant values for β_e (regardless the GMB concentration and detonation velocity) which would roughly represent an uncased charge (β_e=50°) mild plastic (β_e =73°) and strong metal confinement (β_e =85°). Also, it is useful to obtain an approximate relationship between d_{cr}, the shock front curvature radius at r=0 and the β_e value accounting for the confinement properties. Expanding the right hand side of Eq.(16) in the limit sin (β) → 1 we arrive after integration at:

$$d_{cr} \approx 2R_{th} \cos(\beta_e) \qquad (19)$$

where R_{th} is the threshold curvature radius at the peculiar point of the $D(R)$ dependence. This approximate formula agrees fairly well with the results of the numerical integration of Eq.(16) and shows that the critical detonation diameter is proportional to the threshold curvature radius. Thus, d_{cr} depends on the chemical reaction rate through and R_{th} on the confinement properties through the angle β_e.

COMPUTATION RESULTS AND DISCUSSION

The input parameters of the model are listed in Table 1 in our previous work [3]. The constants ν=1 and B=0.02 cm/(μs Mbar) in the burning law (13) are inferred from experimental data [10]. The temperature coefficient β_T is estimated in a traditional way by $\beta_T = E/(2RT_3)$ where E, R and T_3 are the activation energy, the universal gas constant and the reaction products temperature at the ignition time respectively. The effective glass viscosity was chosen arbitrarily (μ1=100 Pa.s), because its effect on the critical detonation diameter is weak if μ1 is much greater than the gelled nitromethane viscosity (2 Pa.s) but still lower than about 5×10^5 Pa.s when the viscous deformation of GMB becomes so slow that heat conduction precludes formation of hot spots during GMB deformation [3]. We studied the effect of GMB size (d_0), weight concentration (x) and shell thickness (h_0), burning rate parameters (B and β_T) and glass viscosity (μ1). For example, Fig. 1 shows the effect of x (%) on a dependence of the detonation velocity D upon the axial radius of curvature of the shock, R_a, with d_0=43.2 μm. Each curve has a limiting particular point, and the threshold curvature radius Rth corresponding to this point decreases as x is increased. The results of computations also show that $R_{th} \sim d_0$ and $R_{th} \sim 1/B$. The effect of β_T is more complicated because even little changes in β_T produce large changes in the shape of the $D(1/R_a)$ curves. the higher β_T the smaller is R_{th} and the detonation velocity deficit. An increase in the glass viscosity from μ1=100 Pa.s to 104 Pa.s and in h_0 from base value 0.52 μm to 3 μm results in a relatively weak effect of μ1 and h_0 on the $D(1/R_a)$ and R_{th} dependencies. However, further increase in μ1 and h_0 enhances the GMB blocking effect and suppresses their sensitization effect [3]. The detonation reaction time π_{CJ} at a relatively high detonation velocity ranges from 0.5 to 1 μs for all mixtures studied and increases to a few μsec as D decreases. In all cases, the detonation reaction zone thickness is significantly smaller than the shock front curvature radius. The unburnt explosive fraction increases as the detonation velocity decreases and reaches a value of about 50% at the detonation propagation limit.

Figure 2 shows the charge diameter effect on D calculated for 43.2 μm GMBs and plastic confinement. The effect of confinement is qualitatively illustrated in fig.3 where one can see that the transition from an uncased charge to a plastic and, especially, to a steel confinement results in a significant decrease of slope of dependence $D(1/d)$ and up to 6-fold decrease in the critical charge diameter. These trends agree with experimental data [1,2].

Figure 4 compares computation results for nitromethane-GMB mixtures with experimental data in a plane dcr - L_p^3/d_0^2 at the same d_0=43.2 μm, 74.4 μm and 102 μm and x_s (ranging from 0.5% to 5%) as in experiments [1,2] (Lp is the GMB spacing). The straight solid line represents an example of an empirical linear correlation between dcr and L^3_p / d^2_0 holding for many GMB-sensitized liquid and emulsion explosives [3]. In the particular case of nitromethane, this correlation reads:

$$d_{cr} = 0.464 + 0.0159(L_p^3/d_0^2) = 0.464 + 0.00832(d_0/\phi 1_0) = 0.464 + 50/A_s \qquad (20)$$

$\phi 1_0$ is the initial GMB volume fraction, dcr and As are measured in mm, and Lp and d_0 in μm. Broken lines in fig 4 correspond to the critical diameters calculated at fixed GMB size. Note, that the GMB volume fraction $\phi 1_0$ decreases along these lines as the parameter L_p^3 / d_0^2 increases or the GMB specific surface As decreases. Figure 4 shows that the calculated critical detonation diameters and effect of GMB size do are in reasonable agreement with the experiments. The computations also show that dcr ~Rth ~1/B so that dcr is inversely proportional to the chemical reaction rate, in agreement with [11]. However, as a whole, we failed to reproduce the correlation (20) because the calculated effect of GMB concentration is weaker than the experimental one, as observed by comparing the slope of the empirical solid line with that of the broken lines corresponding to different do. Thus, the critical detonation diameter is overestimated at large GMB volume fractions, and underestimated at small $\phi 1_0$. This failure is attributed to the behavior of the specific burning surface S_f and its relationship to the initial GMB specific surface As. Let us consider S_f at the ignition time and burning front coalescence instant, $(S_f)ign$ and $(S_f)c$ respectively. For d_{cr} to be proportional to $1/\phi 1_0$, both $(S_f)ign$ and $(S_f)c$ must be proportional to As. However, calculations show that this proportionality holds only for $(S_f)ign$, and that the $(S_f)c$ dependence on As is weaker because the increase in $\phi 1_0$ is coupled with the decrease in the GMB spacing Lp. Taking into account Eq (12), one can show that, at small $\phi 1_0$, the dependence of d_{cr} on $\phi 1_0$ decreases from d_{cr} $1/\phi 1_0$ to d_{cr} $1/\phi 1_0^{1/3}$. This trend is due to the concept of spherical burning fronts diverging from the reaction center which underlie nearly all hot-spot models. Though our model predictions agree reasonably with experiments in many aspects, the description of hot-spot growth stage should be modified to provide a better prediction of the GMB volume fraction effect.

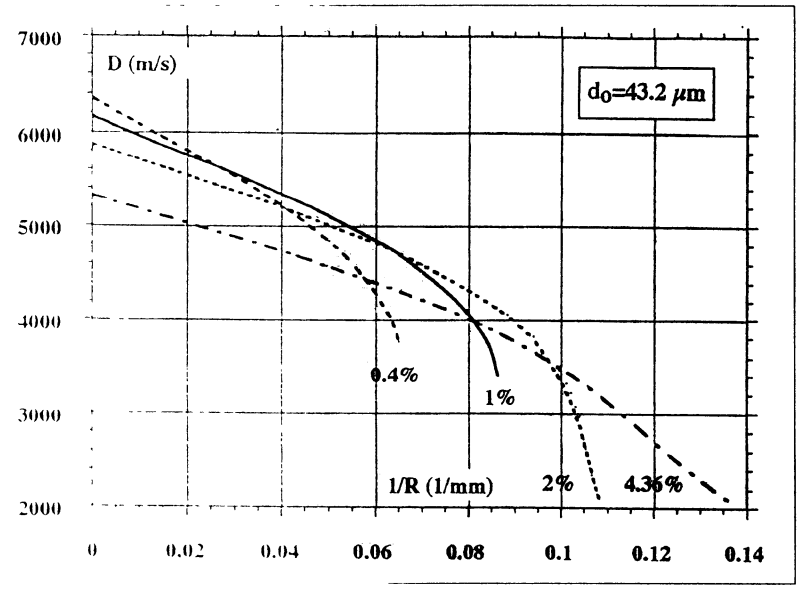

Figure 3. Effect of 43.2 μ diameter GMB mass fraction on dependence of detonation velocity vs. reciprocal of the curvature radius

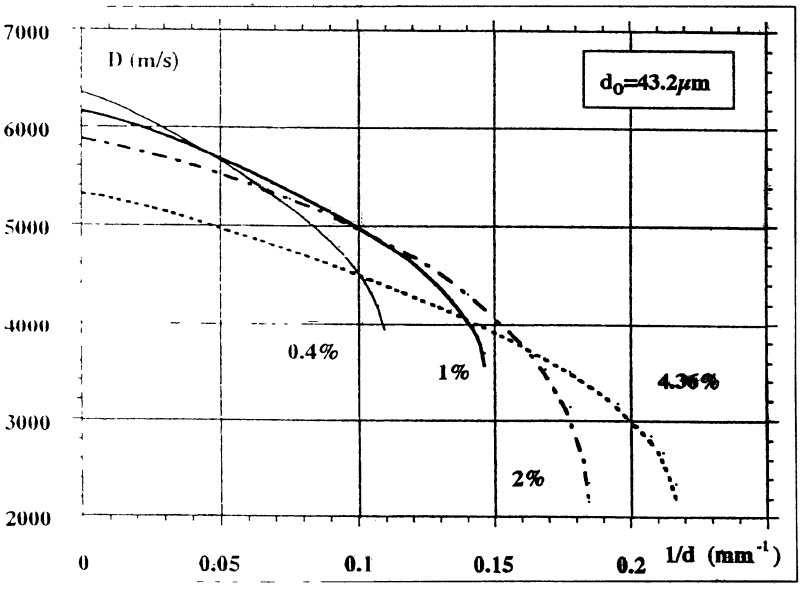

Figure 4. Detonation velocity vs. reversed charge diameter at different GMB mass fraction.

CONCLUSIONS

A model was developed to describe the detonation reaction zone in GMB-sensitized liquid explosives. The heat release rate was defined as the product of the normal

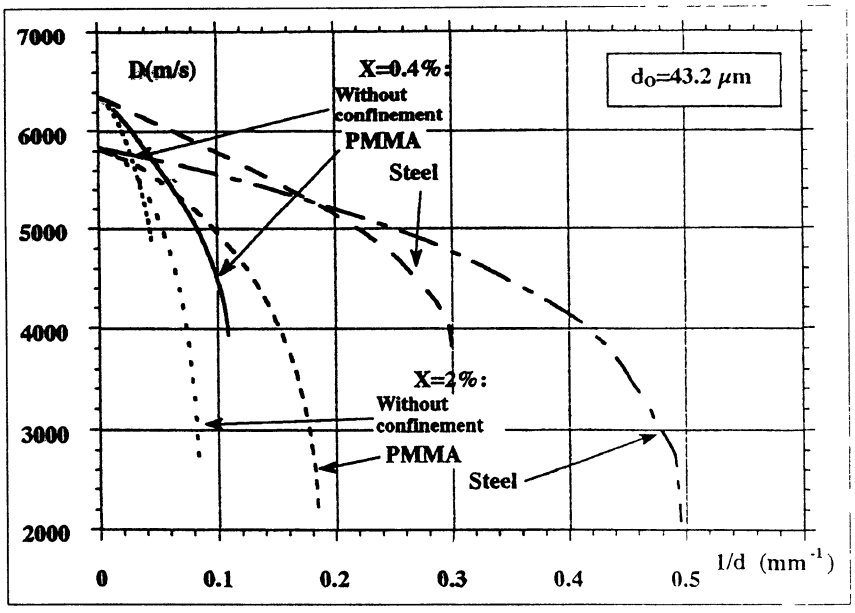

Figure 3. Effect of confinement on dependence of detonation velocity vs reciprocal of charge diameter

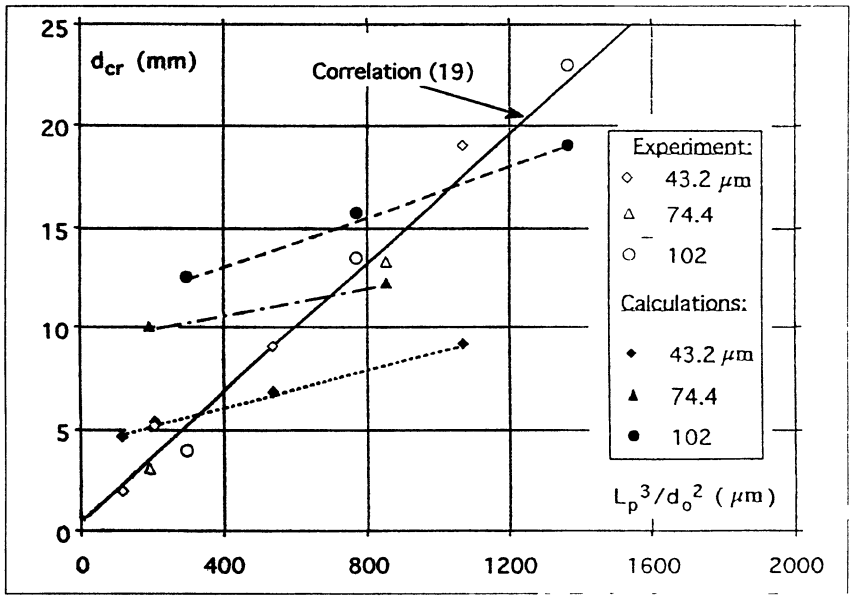

Figure 4. Comparison of calculated critical detonation diameters (solid points) with experimental ones shown by similar open points in a plane d_{cr}-L^3_p / d^2_o

regression rate and specific surface of the burning fronts taking into account the physical processes of GMB deformation, ignition of the explosive and evolution of burning waves diverging from individual GMBs. All the input parameters of the model have clear physical meaning and, in general, can be measured directly. The model was used to analyze the problem of the critical detonation diameter in GMB sensitized explosives. The effect of heterogeneities on the critical detonation diameter and on the detonation velocity-charge diameter dependence was calculated by using the quasi-one-dimensional approach proposed by Bdzil. The computed values of critical diameters and effect of GMB size on the critical diameter were found to be in reasonable agreement with the experimental ones. However, the computed effect of GMB concentration is weaker than the experimental one. The analysis shows that this disagreement cannot be eliminated by varying the model input parameters and is due to the concept of diverging spherical flame fronts widely used in many models considering hot-spot growth in reactive inhomogeneous media. With proper modifications, the model of reaction zone proposed in the present paper can be used for quantitatively predicting the charge diameter and confinement effects on the detonation velocity in the case of GMB-sensitized explosives. In addition, this model can be used to solve the inverse problem of kinetic data determination based on measured critical diameters and charge diameter effect for heterogeneous explosives

REFERENCES

(1) Presles H.-N., Campos J., Heuze O., Bauer P. Effect of microballoons concentration on the detonation characteristics of nitromethane-PMMA mixture // Proc. Ninth Symp. (Int.) on Detonation. ONR 113291-7, 1989. P.925-929.

(2) Presles H.-N., Vidal P., Khasainov B.A., Ermolaev B.S. Influence of glass microbal loons size on the detonation of nitromethane based mixtures // XIV ICDERS. 1993. Coimbra, Portugal.

(3) Khasainov B.A., Ermolaev B.S., Presles H.-N. Shock wave initiation of chemical reaction in liquid high explosives sensitized by glass microballoons // Preprints of Tenth Int. Symp. on Detonation. 1993. Boston,

(4) Bdzil J.B. Steady-state two-dimensional detonation // J. Fluid Mech. 1981. V. 108. P. 195.

(5) Bdzil J.B., Stewart D.S., Modeling of two dimensional detonation with detonation shock dynamics // Physics of Fluids A.1988. V. 1. P. 1261-1267.

(6) Zeldovich Ya.B., Kompaneetz S.A. Theory of Detonations. NY Academic Press. 1960.

(7) Nigmatulin R.I. Dynamics of multiphase flows // 1987. Moscow, Nauka. V. 1. P. 464.

(8.) Mader C.L , Shaw M S. User's manual for SIN // LASL 1978 LA-7264-M.

(9) Cowperthwaite M., Shaw R. Cv(T) equation of state for liquids Calculation of the shock temperature of carbon tetrachloride, nitromethane and water in the 100 kbar region. J. Chem.Phys. 1970. V 53 P 555-560.

(10) Rice S.F., Foltz F. Very high pressure combustion. reaction propagation rates of nitromethane within a diamond anvil cell // Comb and Flame. 1991 V 87 P 109-122.

(11) Leiper G.A., Kirby I I A method of parameterizing hydrocode kinetic models for non-ideal explosives based on the variation of detonation velocity with charge diameter // Shock waves in condensed media. Edited by Gupta. 1986. Plenum, NY. P. 917-922.