

THE EFFECT OF Al_2O_3 PHASE TRANSITIONS ON DETONATION PROPERTIES OF ALUMINIZED EXPLOSIVES

Sergey B. Victorov

Moscow Engineering Physics Institute (State University)

31 Kashirskoe chaussee, Moscow 115409, Russia

e-mail: sb_victorov@mail.ru

We have computed the detonation properties of HMX–Al, RDX–Al, and BTNEN–Al compositions using our thermochemical TDS code. The calculations are based on reliable statistical-mechanical EOS model for the fluid detonation products and semi-empirical EOS for carbon nanoparticles and for the solid and liquid phases of Al and Al_2O_3 . It is shown that the Al_2O_3 melting may occur in the detonation products of the investigated compositions at intermediate initial densities of HE. This phase transition may affect the detonation performance and can be detected experimentally. We suggest a simple experimental study that might answer an important question, namely, whether the Al reacts within the reaction zone of a detonation wave. If this question is solved positively, it will be also possible to estimate the extent of the Al oxidation.

INTRODUCTION

Detonation of aluminized high explosives (HE) is extensively studied experimentally and theoretically since the middle of the 20th century. On the one hand, these studies are of practical interest because introduction of aluminum into explosives can improve their detonation performance. On the other hand, the researches are of great scientific interest because detonations of HE with Al additives give a number of surprises and, as a consequence, there are unresolved problems in understanding the aluminum behavior in detonation. A detailed review on these problems is given in Ref. 1, which critically analyzes the contemporary notions of aluminum behavior in HE detonation.

The key theoretical question is whether the Al reacts in the reaction zone of a detonation wave or at a later time. The majority of researchers believe that for the case of powerful aluminized HE, aluminum behaves as an inert additive in the reaction

zone and is oxidized only in expanding detonation products. However, there are supporters of the opposite viewpoint stating that Al participates, at least partially, in the chemical reaction upstream the Chapman–Jouguet (CJ) plane. The latter researchers generally make their conclusion by using thermochemical codes based on the CJ thermodynamic detonation theory. They calculate the detonation parameters of powerful aluminized HE and estimate the extent of Al oxidation, i.e. the fraction of aluminum reacted within the reaction zone of a detonation wave, by adjusting the Al burnt fraction to provide the best agreement between calculated and measured detonation velocities.

The estimations of Al burnt fraction being obtained in such a way are often contradictory. For example, Imkhovik and Soloviev² have interpreted their results on RDX–Al compositions as a support of the standpoint that aluminum does not react in the reaction zone of a detonation wave. The value of 40% obtained by Hobbs and Baer³ for the Al burnt fraction in HMX–Al

compositions is, oppositely, rather high. The results of Cowperthwaite⁴ for RDX–TNT–Al yield even 70%.

There are two main reasons of these discrepancies. Firstly, the researchers apply differing equations of state (EOS) to describe the thermodynamics of the detonation products. Hence, the results may differ from each other, especially taking into consideration the fact that the calculated detonation velocity and pressure of powerful aluminized HE are known to depend on the Al burnt fraction rather weakly^{2–5}. Secondly, for the case of aluminized HE, the CJ detonation theory may become inapplicable itself because its assumption of instantaneous thermodynamic equilibrium of the detonation products breaks down for non-ideal explosives. One can clearly see this, e.g. for aluminized explosive oxidizers such as ammonium nitrate. More sophisticated detonation theory should be used to modeling non-ideal detonations as was done, e.g., by Howard *et al.*⁶ They implement a Wood-Kirkwood kinetic model⁷ with finite rate laws for the slowest chemical reactions. Thus, it is very difficult or even impossible to make a reliable conclusion about the extent of Al oxidation within the reaction zone on the basis of CJ thermochemical calculations.

Nevertheless, in this work we perform thermochemical computations of the detonation parameters of three powerful aluminized HE, namely, HMX ($C_4H_8N_8O_8$), RDX ($C_3H_6N_6O_6$), and BTNEN ($C_4H_4N_8O_{14}$). The calculations are based on the CJ detonation theory and are done by our thermochemical TDS code⁸. Our purpose is to search for a way that may answer the key question, i.e. whether the Al reacts in the reaction zone of a detonation wave of powerful HE. It is appropriate to emphasize here that we do not plan to exactly answer this question in the present work, this is practically impossible within the framework of thermodynamic modeling on the basis of the CJ detonation theory as

mentioned above. However, we hope that the results of thermodynamic modeling will allow us to suggest a simple experimental research that might well solve the key question.

The main idea lies in the following. If the aluminum is oxidized, at least partially, within the reaction zone of a detonation wave, the detonation products will contain solid or liquid aluminum oxides whose formation are much more thermodynamically favorable than that of fluid (gaseous) aluminum oxides. Assuming that the condensed aluminum oxide is Al_2O_3 , we will perform thermochemical calculations in order to determine whether there are the initial conditions (e.g., the values of the charge density) under which the detonation parameters lie close to the melting curve of Al_2O_3 . In this case, the Al_2O_3 phase transition may occur in the detonation products near the detonation front and affect the detonation performance. If such the initial conditions are found, we will then investigate the effect of the Al_2O_3 phase transition on the detonation properties of HE. Provided this investigation shows that the phase transition strongly affects the detonation parameters so that the effect can be detected experimentally, a suggestion on the experiments required might be then formulated.

If the future experimental research does not confirm the predicted effect of the Al_2O_3 phase transition on the HE detonation behavior, then we will not be able to conclude whether the aluminum is oxidized within the reaction zone. However, if the experimental findings are in agreement with the predicted effect and they cannot be a result of factors other than the phase transition of the aluminum oxide, we will confidently be able to state that the aluminum does react there.

HMX/RDX and BTNEN were chosen for the present study because their

detonation produces either relatively small amount of condensed carbon (HMX/RDX at high initial densities) or no carbon at all (BTNEN at any initial density and HMX/RDX at intermediate and low initial densities). Hence, possible phase transitions of condensed carbon may affect the detonation parameters only slightly and the effect of Al₂O₃ phase transitions (if any) can be recognized more reliably. Furthermore, there are recent experimental data on detonation performance of HMX–Al⁹ and BTNEN–Al¹⁰ compositions.

As one can see below, we are succeed in finding the initial conditions under which the Al₂O₃ phase transitions may occur in the detonation products of the aluminized compositions being investigated. The calculations predict that the effect of the phase transitions may be rather strong and we suggest an experimental study, which might let us know whether the aluminum reacts within the reaction zone and even estimate the Al burnt fraction.

FORMULATION

It is assumed that molecules i and j of the fluid phase of detonation products (N₂, N, H₂O, CO₂, CO, NH₃, NO, CH₄, O₂, O, H₂, H, and OH) interact via a spherically symmetric, modified Buckingham (Exp-6) potential

$$\varphi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij} - 6} \{ 6 \exp[\alpha_{ij}(1 - r/r_{m,ij})] - \alpha_{ij} (r_{m,ij} / r)^6 \}, \quad (1)$$

where r is the intermolecular separation, ε_{ij} is the depth of the attractive well, $r_{m,ij}$ is the position of the potential well minimum, and α_{ij} controls the stiffness of the repulsive part of the potential. Such the potentials are especially suitable to describe intermolecular interactions at high pressures and high temperatures, i.e. under conditions relevant to detonation problems.

For strongly attracting molecules (H₂O and NH₃ in this work), we use Exp-6 potentials with a temperature-dependent well depth

$$\varepsilon_{ii}(T) = \varepsilon_{0,ii}(1 + \lambda_{ii} / T), \quad (2)$$

where T is the temperature, and $\varepsilon_{0,ii}$ and λ_{ii} are the constants (for non-polar molecules $\lambda_{ii} = 0$). The dependence (2) was suggested by Ree¹¹ to simulate the average electrostatic effects of orientation on the intermolecular potential.

By now, there are a number of reliable statistical-mechanical theories, which produce the excess thermodynamic properties of a pure (one-component) fluid in excellent agreement with Monte Carlo (MC) and molecular dynamics simulations for different types of intermolecular potentials including the Exp-6 form. In this work we use the HMSA/MC EOS of Fried and Howard¹², which is based on the hypernetted-mean spherical approximation integral equations for pair distribution functions¹³ and MC simulation data. We find that HMSA/MC and our KLRR/C EOS⁸ deviates from each other extremely slightly in the region of thermodynamic states being of interest in the present work. Since KLRR/C was derived from another reliable statistical-mechanical theory¹⁴⁻¹⁵, its good agreement with HMSA/MC confirms once again a high accuracy of both EOS.

The post-detonation products are hot reactive mixtures. To calculate properties of such mixtures, we use the improved van der Waals one-fluid (vdW1f) model¹⁶, which assumes a mixture of chemical species, interacting via potentials (1), to be a hypothetical one-component fluid with an effective Exp-6 potential. The composition-dependent parameters of this effective potential are given by:

$$\alpha = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \alpha_{ij} \varepsilon_{ij} (r_{m,ij})^3 / [\varepsilon (r_m)^3],$$

$$\varepsilon = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \varepsilon_{ij} (r_{m,ij})^3 / (r_m)^3,$$

$$r_m = \left[\sum_{i=1}^n \sum_{j=1}^n x_i x_j (r_{m,ij})^3 \right]^{1/3}, \quad (3)$$

where the summation extends over all ij pairs, n is the number of the components, and x_i is the mole fraction of species i .

One-component calculations are much simpler than the implementation of a multicomponent theory. This justifies for using the vdW1f model. Ree¹⁶, who is the author of the α -mixing rule [the first expression in (3)], has shown that the one-component model (3) produces excellent agreement with two-component MC simulation data on He–H₂ mixtures. Furthermore, there are several theoretical researches whose results can be considered as a support of the vdW1f model.

Since the effective potential (3) is temperature-dependent because of (2), we use our THEOSTAR-T model that simply extends the original Byers-Brown's THEOSTAR expressions¹⁷ to the case of a temperature-dependent Exp-6 potential.

The like-pair Exp-6 parameters α_{ii} , $r_{m,ii}$, $\varepsilon_{0,ii}$, and λ_{ii} for the fluid detonation products were determined mostly by matching experimental Hugoniot data and available results of static experiments. The Exp-6 parameters used in this work are listed in Table 1. A few potentials were taken from the works of other researchers. In these cases the corresponding references are given in Table 1. The Hugoniot of shock compressed liquids, N₂, H₂O, CO₂, NH₃, H₂, and O₂, which were calculated by TDS with the potentials from Table 1, are shown in Fig. 2 of Ref. 8 and are in good agreement with the experimental data.

TABLE 1. EXP-6 PARAMETERS.

Species	$\varepsilon_{0,ii}$, K	$r_{m,ii}$, m ⁻¹⁰	α_{ii}	λ_{ii} , K
N ₂	100.6	4.25	12.3	0
N	120.0	2.65	10.4	0
O ₂	96.2	3.79	14.7	0

O	277.0	2.57	11.5	0
NO	182.9	3.70	13.0	0
CO ₂	247.2	4.26	13.4	0
CO	110.0	4.13	14.0	0
CH ₄	154.1	4.22	13.5	0
H ₂ ^{Ref. 18}	37.0	3.55	10.8	0
H	20.0	1.40	13.0	0
OH ^{Ref. 19}	80.0	3.29	13.0	0
H ₂ O ^{Ref. 18}	188.0	3.24	13.3	496.0
NH ₃ ^{Ref. 18}	96.7	3.95	12.9	117.0

The Exp-6 parameters for unlike-pairs ($i \neq j$) can be formally expressed as

$$r_{m,ij} = k_{ij}(r_{m,ii} + r_{m,jj}) / 2,$$

$$\varepsilon_{ij} = l_{ij}(\varepsilon_{ii} \varepsilon_{jj})^{1/2},$$

$$\alpha_{ij} = m_{ij}(\alpha_{ii} \alpha_{jj})^{1/2}, \quad (4)$$

in terms of like-pair parameters and the correction factors k_{ij} , l_{ij} , and m_{ij} which are expected to be close to unity and can be fixed if appropriate theoretical or experimental data are available. Otherwise, we set $k_{ij} = l_{ij} = m_{ij} = 1$ that reduces (4) to the Lorentz–Berthelot combination rule²⁰.

All thermodynamic quantities of the fluid phase at a given temperature T and volume V can be represented as the sum of an ideal and excess contributions. The ideal contribution is equal to the corresponding quantity of the ideal gas at the same T and V . The excess contribution depends on intermolecular interactions only and is computed from the THEOSTAR-T model. To calculate the ideal contribution, in this work we employ the polynomial fits that accurately approximate the tabular thermodynamic data²¹.

The condensed graphite and diamond nanoparticles, which may be formed in the detonation products, are treated by our model⁸. This model is based on the carbon EOS model of van Thiel and Ree²² and has simple correction terms that allow one to take into account the effect of the small size of carbon particles on their thermodynamics. We refer Ref. 8 for more details.

The following species containing Al are being considered in this work: solid and liquid Al, and solid and liquid Al₂O₃. To describe their thermodynamics, we implement semi-empirical EOS in a Gruneisen-like form suggested by Molodets²³. The EOS of condensed Al and solid Al₂O₃ were calibrated by matching available thermal and shock-wave data. For liquid Al₂O₃ there is a lack of any high-pressure experimental data so that the EOS parameters were chosen to match the density of the known atmospheric isobar as well as high-pressure values estimated from the solid EOS and the melting point data.

The obtained EOS model of Al₂O₃ predicts the considerable effect of pressure on melting point of approximately 130 K/GPa. The calculated melting temperature of Al₂O₃ reaches, e.g., 4400 K at 15.5 GPa (while the known melting temperature is 2327 K at 1 atm). Such the behavior of the melting curve makes it possible to hope that the Al₂O₃ phase transitions may really occur in the detonation products of powerful aluminized HE and affect the detonation performance. Indeed, in the case that Al reacts (at least partially) within the reaction zone, detonation may produce the solid Al₂O₃ at high initial densities of HE due to high detonation pressure and relatively low detonation temperature. The liquid Al₂O₃ may be produced in the detonation products at low initial densities of HE, where detonation pressures are lower and detonation temperatures are higher. As regards Al₂O₃ melting, it may occur and affect the detonation performance at intermediate initial densities of HE.

The EOS of liquid Al₂O₃ used in this work should not be viewed as enough reliable because it was constructed under conditions of the lack of high-pressure data for this species including the melting curve data. Among the thermodynamic properties of Al₂O₃, the location of the melting curve at high pressures is one of the most important for the purposes of the present

work. We believe, however, that the predicted effect of pressure on melting point may be close to the reality. Braithwaite *et al.*²⁴ have recently developed an EOS model for the melt and solid phases of diopside (CaMgSi₂O₆) that accurately reproduces the known high-pressure properties of this dense material. The effect of pressure on melting point of diopside calculated in their work is approximately 180 K/GPa, i.e. is even higher than our value for Al₂O₃. Howard *et al.*⁶ have implemented a modified Murnaghan EOS for solid and liquid Al₂O₃ in modeling the detonation of aluminized compositions based on high-density HMX. They find that Al₂O₃ is in the solid state during the detonation. Thus, their EOS model is likely to predict considerable increasing of the Al₂O₃ melting temperature at high pressures.

We use below the CJ theory to compute the detonation properties of aluminized compositions. The CJ point must lie on a reactive Hugoniot

$$E = E_0 + (P + P_0)(V_0 - V) / 2. \quad (5)$$

The subscript 0 refers to the initial pre-detonation state of an explosive composition; quantities E , P , and V represent the post-detonation state behind the detonation front. Among all the points, which satisfy the Hugoniot (5), we select the CJ point as one that corresponds to the minimum of entropy of the detonation products (or the minimum of detonation velocity).

If phase transitions occur behind the detonation front, the entropy may have multiple local minima. For this reason, we have developed a special numerical solver that guarantees that all local minima of the entropy along the reactive Hugoniot will be found so that the global entropy minimum (the CJ point) will be correctly computed. This solver has been incorporated into the TDS code.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the detonation velocity, D , on the Al content (weight %) for HMX–Al compositions at the initial density of HMX, $\rho_{0,HE}$, of 1.81 g/cm^3 . The lines are the results of our calculations. The symbols are the experimental data of Gogulya *et al.*⁹, who varied both the Al content and the Al particle size from $0.5 \mu\text{m}$ to $150 \mu\text{m}$.

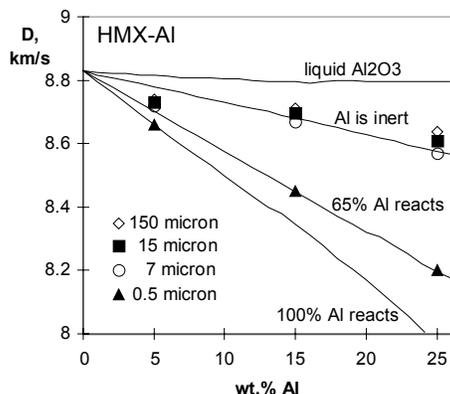


FIGURE 1. D-vs-AL CONTENT FOR HMX-AL. $\rho_{0,HE} = 1.81 \text{ G/CUB.CM}$.

The values of D calculated on the assumption that the Al is inert within the reaction zone (the line labeled «Al is inert» in Figure 1) are in good agreement with the experiments except for the case of the smallest Al particles. The calculations find that the unreacted Al is in the liquid state during the detonation.

The line labeled «100% Al reacts» shows the results of completely equilibrium calculations that correspond to the case that the Al is completely oxidized within the reaction zone. These calculations predict that the Al_2O_3 is in the solid state behind the detonation front. The computed effect of Al content on D is more considerable than it was measured for an Al particle size of $0.5 \mu\text{m}$. We find that a theoretical D -vs- wt.\% Al dependence is in good agreement with the experiments for the smallest Al particles at the Al burnt fraction of 65%. The corresponding results are shown in Figure 1 as a line labeled «65% Al reacts».

These calculations also predict the formation of the solid Al_2O_3 and the liquid state of the unreacted Al.

A line labeled «liquid Al_2O_3 » represents the results obtained on the assumption that the Al completely reacts but the liquid Al_2O_3 is formed behind the detonation front instead of a solid. One can see that in this case D is practically independent on the Al content.

Taking into account the fact that the small size of Al particles may facilitate their oxidation during the detonation, the results presented in Figure 1 could justify the following standpoint. The Al reacts in a large extent (about 65%) for the investigated HMX–Al compositions with the Al particle size of $0.5 \mu\text{m}$ while the Al is mostly inert for larger particles. We do not make, however, such unambiguous conclusion because there may be a variety of other factors that can explain the measured rapid decrease in D with increasing the Al content for the smallest particles. For example, this may be excessive Al_2O_3 coating of the Al particles, a possible failure of the CJ theory and so on.

We do not present the computed results for RDX–Al at high $\rho_{0,HE}$ since they are practically the same as those of HMX–Al.

The results of our calculations for BTNEN–Al compositions at $\rho_{0,HE} = 1.90 \text{ g/cm}^3$ are shown in Figure 2. The recent experimental data of Gogulya *et al.*¹⁰ for 15 wt.% Al are also presented there. All the labels in Figure 2 are done in the same manner as in Figure 1.

The calculations assuming that the Al is inert are in excellent agreement with the experiments for the largest Al particles. The equilibrium calculations again predict the formation of the solid Al_2O_3 , but now the «100% Al reacts» curve lies near the «Al is inert» one and slightly beyond the experimental results. The D -vs- wt.\% Al

dependence calculated for the case of the liquid Al_2O_3 is well above the experimental points and shows a rapid increase in D with increasing the Al content.

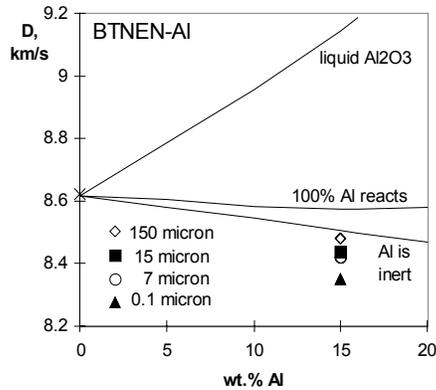


FIGURE 2. D -vs-AL CONTENT FOR BTNEN-AL. $\rho_{0,HE} = 1.90 \text{ G/CUB.CM}$.

Thus, we conclude that detonation of powerful aluminized HE may produce the solid Al_2O_3 at high initial densities of HE in the compositions. This conclusion is likely to be consistent with the results of Howard *et al.*⁶ but is in contrast to more common standpoint that behind the detonation front the Al_2O_3 (if any) is a liquid.

Below we present and discuss the calculated detonation parameters of aluminized compositions in a wider range of HE initial densities including the low and intermediate values of $\rho_{0,HE}$.

The detonation velocities of RDX-Al mixtures with different Al content (from 0 to 25 wt.%) computed for an ideal case (under the assumption of equilibrium, i.e. the Al completely reacts in the reaction zone) are represented in Figure 3 as plots vs $\rho_{0,HE}$. The symbols are the experimental values of D for pure RDX, they are in good agreement with our calculations (the line labeled «100/0»).

At $\rho_{0,HE} < \rho_{0,HE,*}$ (where $\rho_{0,HE,*} = 1.26, 1.34, 1.41, \text{ and } 1.48 \text{ g/cm}^3$ for the mixtures containing 10, 15, 20, and 25 wt.% Al, respectively) the liquid Al_2O_3 is formed in the detonation products. Within the region

$\rho_{0,HE,*} < \rho_{0,HE} < \rho_{0,HE,*} + \Delta\rho_{0,HE,*}$, the Al_2O_3 phase transition occurs in the detonation products and the D -vs- $\rho_{0,HE}$ dependencies have a break in their slopes. Both $\rho_{0,HE,*}$ and $\Delta\rho_{0,HE,*}$, i.e. the position and the width (in the $\rho_{0,HE}$ -axis) of the phase transition regions decrease with decreasing the Al content in the compositions. There are no Al_2O_3 phase transitions in the detonation products at $\rho_{0,HE} > \rho_{0,HE,*} + \Delta\rho_{0,HE,*}$. The solid Al_2O_3 is formed there.

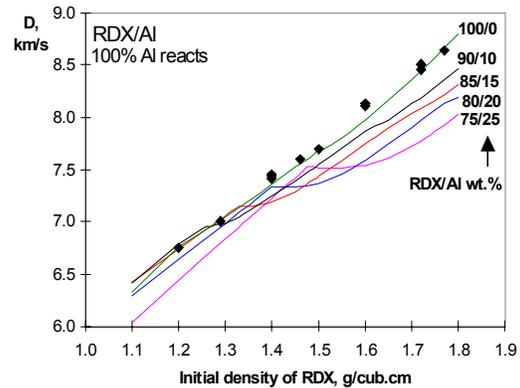


FIGURE 3. D -vs- $\rho_{0,HE}$ FOR RDX/AL. THE AL COMPLETELY REACTS.

A thing which is of more practical interest, namely, the effect of the extent of Al oxidation on the detonation velocity of the RDX/Al-75/25 wt.% mixtures is shown in Figure 4 for the Al burnt fraction of 25, 50, 75, and 100 wt.%. The curve labeled «100%» corresponds to the complete Al oxidation and is the same as in Figure 3.

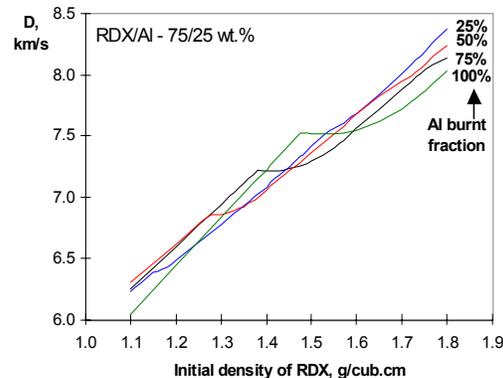


FIGURE 4. D -vs- $\rho_{0,HE}$ FOR RDX/AL - 75/25 WT.%.

There is a decrease in both $\rho_{0,HE,*}$ and $\Delta\rho_{0,HE,*}$ with decreasing the Al burnt fraction. So, for the Al burnt fraction of 100, 75, 50, and 25 wt.% the $\rho_{0,HE,*}$ is 1.48, 1.38, 1.28, and 1.16 g/cm³, respectively, and the $\Delta\rho_{0,HE,*}$ is 0.26, 0.17, 0.10, and 0.04 g/cm³, respectively. Thus, the predicted region of HE initial densities, within which the D -vs- $\rho_{0,HE}$ dependence may have a break in the slope, is enough wide to be experimentally detectable if the Al burnt fraction is about 35-40% or higher.

Since a HMX molecule has the same balance of the chemical elements as that of RDX, the results calculated for HMX–Al and RDX–Al deviate only slightly from each other due to a minor difference in their heats of formation. For this reason, the results for HMX–Al are not presented here.

The calculated results for BTNEN–Al 75/25 wt.% compositions are similar to those of RDX/HMX–Al with the same Al content. At a fixed Al burnt fraction the region of the Al₂O₃ phase transition is located at higher $\rho_{0,HE}$ than for the case of compositions based on RDX/HMX. So, for the Al burnt fraction of 50% the value of $\rho_{0,HE,*}$ is 1.57 g/cm³ (see Figure 5) as compared to 1.28 g/cm³ for RDX–Al.

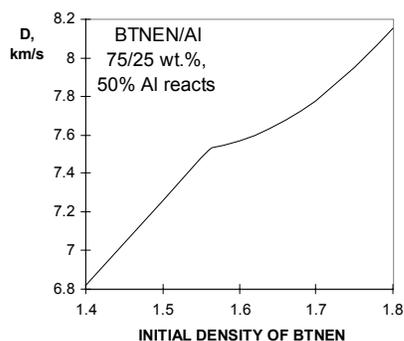


FIGURE 5. D -vs- $\rho_{0,HE}$ FOR BTNEN/AL - 75/25 WT.%, 50% AL REACTS.

It is appropriate to mention here the following. For the case that $\rho_{0,HE}$ lies within the region of the Al₂O₃ phase transition, the calculations predict an

unusual two-front structure of the detonation wave with the second sonic plane located in the rarefaction wave. We have already predicted such the structure for carbon-rich HE in our earlier papers (e.g., Ref. 25) and called it an *anomalous* mode of detonation. The anomalous mode of detonation is caused by the graphite-to-diamond transition behind the detonation front. Now we see that a similar detonation structure may occur due to another phase transition, namely, the Al₂O₃ melting.

We suggest careful measurements of the D -vs- $\rho_{0,HE}$ dependencies for aluminized powerful HE containing about 25-30 wt.% fine Al particles. Explosives with relatively small content of carbon should be chosen in order to avoid the effect of the graphite-to-diamond transition or other phase transitions of the condensed carbon on D . RDX/HMX–Al and especially BTNEN–Al might be the first candidates for this experimental study. The experiments should reveal whether a break in the D vs $\rho_{0,HE}$ slope really occurs.

The position of the beginning of the phase transition region in the $\rho_{0,HE}$ -axis (i.e., the value of $\rho_{0,HE,*}$) is rather sensitive to the Al₂O₃ EOS model. The EOS of liquid Al₂O₃ used in this work is possibly too rough due to the lack of high-pressure data for this material. For this reason, the Al₂O₃ phase transition may occur in the detonation products at HE initial densities that differ from ones predicted in the present work. That is why we suggest further experimental studies for the case that the first series of the measurements fails in the predicted range of HE initial densities. Moreover, if a break in the D -vs- $\rho_{0,HE}$ slope is not detected over a wide range of $\rho_{0,HE}$ for, e.g., BTNEN–Al or HMX/RDX–Al, it would be reasonable to investigate the compositions based on other explosives. Such an approach will allow one to cover a wider range of thermodynamic states in searching for the Al₂O₃ phase transition.

CONCLUSION

In this work we have calculated the detonation properties of HMX–Al, RDX–Al, and BTNEN–Al compositions using our thermochemical TDS code and the CJ detonation theory. The calculations were based on reliable statistical-mechanical EOS model for the fluid detonation products and semi-empirical EOS for carbon nanoparticles and for the solid and liquid phases of Al and Al₂O₃.

For the case that the Al reacts (at least partially) during the detonation, the calculations predict the formation of the solid Al₂O₃ in detonation products of the investigated HE–Al compositions with high initial densities of HE. It is more commonly considered that Al₂O₃ is in the liquid state. We find that the liquid Al₂O₃ may be produced by detonations at low initial densities of HE. It is shown that the Al₂O₃ melting may occur in the detonation products at intermediate initial densities of HE and this phase transition may affect the detonation performance. For example, this transition would cause a break in the D vs $\rho_{0,HE}$ slope that can be detected experimentally.

We suggest careful measurements of the D vs $\rho_{0,HE}$ dependencies for aluminized powerful HE containing about 25-30 wt.% fine Al particles. Explosives with relatively small content of carbon should be chosen in order to avoid the effect of the graphite-to-diamond transition or other carbon phase transitions on D . The compositions investigated in the present work might be the first candidates for this experimental study. The experiments should reveal whether a break in the D -vs- $\rho_{0,HE}$ slope really occurs.

If the experimental research does not detect breaks in the D -vs- $\rho_{0,HE}$ slope, this will not, however, mean that the Al does remain an inert during the detonation. There may be a variety of reasons of the failure of the experiments including the case that our EOS of liquid Al₂O₃ is

possibly too rough due to the lack of high-pressure data for this material.

However, if the experiments are successful and a break in the D -vs- $\rho_{0,HE}$ slope is detected, we will be practically sure that the Al does react within the reaction zone. In this case, it will be also possible to estimate the extent of the Al oxidation from the measured width (in the $\rho_{0,HE}$ -axis) of the region where the D -vs- $\rho_{0,HE}$ slope is broken.

In any case, the suggested experiments will be very useful for further investigating the kinetics of the Al oxidation in detonations and for the refinement of EOS models for the liquid and solid Al₂O₃.

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