Dependence of the Diamond Phase Content in Condensed Detonation Carbon on Trinitrotoluene Concentration in the Explosive Mixture Trinitrotoluene/Diethanolamine Dinitrate

N. V. KOZYREV[1], P. I. KALMYKOV[1,2], A. G. VAKUTIN[1], K. A. SIDOROV[2,3]

[1]*Institute for Problems of Chemical and Energetic Technologies, Siberian Branch, Russian Academy of Sciences, Biysk, Russia*

E-mail: kozyrev@ipcet.ru

[2]*Federal Research and Production Centre ALTAI, Biysk, Russia*

[3]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

Abstract

The dissolution of trinitrotoluene (TNT) in a low-melting nitramine, diethanolnitramine dinitrate (DINA), was studied, and a phase-state diagram for the TNT/DINA system was built. The enthalpy of TNT dissolution in DINA within the temperature range 55−75 °C was measured. The yields of condensed carbon (CC), detonation nanodiamonds (DNDs) and DND content in CC versus the composition of TNT/DINA cast melts upon detonation in a blasting chamber were experimentally studied. The yield of CC was found to linearly decline with decreasing TNT content in the composition, with the content of diamond phase in CC going through the maximum. The highest yield of DNDs was achieved when the TNT content in the mixture was close to the eutectic (~40 mass %).

Keywords: TNT, DINA, enthalpy of dissolution, detonation synthesis, detonation nanodiamonds

INTRODUCTION

The synthesis of detonation nanodiamonds (DND) is studied most thoroughly for trinitrotoluene−hexogen melts. In was reported in [1] that DND synthesis was carried out for the first time as long ago as in 1963. Pure trinitrotoluene and its mixtures with hexogen in the ratios of 50 : 50, 40 : 60, 30 : 70 were studied using the charges in the form of discs, balls, cylinders. The major regularities of the synthesis were studied, and a qualitative model of the phenomena determining DND synthesis was built up in [2]. The versions from pure trinitrotoluene (TNT, trotyl) to its mixture with hexogen up to the ratio of 30 : 70 were studied with a step of 10 %. It was discovered that the highest DND yield is provided by melts with the mass ratio of components 50 : 50. In addition, the mixtures of toluene with octogen in the ratios of 70 : 30 and 30 : 70 were tested. The effect of trotyl content in the charges with different content of explosive substances (ES) was studied in detail in [3]. Both pure trotyl and its mixtures with hexogen, octogen and tetranitropentaerythriol (TEN) were investigated. It was established that the maximal yield is achieved with trotyl content ~60 % for mixtures with hexogen and octogen, and at 65−70 % for mixtures with TEN. A number of works dealt with the studies of the synthesis from TNT−hexogen melts

in the region of the highest DND yield [4−6]. For instance, TNT-hexogen 50 : 50 system was studied in [4], while a 65 : 35 system was studied in [5]. The effect of the mass of water shell at the charge surface on DND yield from the TNT/hexogen mixture (55.5 : 44.5) was described in [6].

The yield of DND from pure TNT is rather small, so it is urgent to search for other, more powerful explosive substances (ES) allowing an increase in the amount of resulting diamonds when added to trotyl. For instance, in [7] the melts of TNT with triaminotrinitrobenzene (TATB) (50 : 50), with nitroguanidine (NQ) (50 : 50), and with hexogen (40 : 60) were studied. Cast and pressed charges of pentolite (TNT−TEN, 50 : 50) were used to determine the yield of DND from the explosion in various gas media [8]. Polycyclic explosive nitramines VSNMKh (2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclo[3,3,0]octane) and Avrora (4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitan) as additives to trotyl were studied by the authors of [9]. These substances are close in powder to octogen but they carry smaller oxygen balance, so they allow a slight increase in the yield of DND in comparison with hexogen and octogen in the case of the optimal content in mixture 60−70 %. Even lower oxygen balance is characteristic of benzotrifuroxan (BTF), which is anhydrous ES close in power to hexogen and octogen. A melt of TNT−BTF (60 : 40) was studied in [10]. The use of BTF as an additive to trotyl also allows an increase in the yield of DND in comparison with octogen.

At present, one of the most powerful ES is hexanitrohexaazaisowurtzitane (CL-20), exceeding both hexogen and octogen in the density and rate of detonation. Its use as an additive to trotyl allows one to increase the density of the charge, and therefore the detonation pressure. In this connection, one may expect a substantial increase in DND yield from the detonation of these compositions. This assumption was confirmed in [11], where the results of the detonation synthesis of DND from pressed and cast TNT−CL-20 charges at a ratio of 60 : 40 and 70 : 30 using the ε-modification of CL-20 were described. The average yield of DND in comparison with similar TNT-hexogen melts increased from 9 to 9.9−10.4 %.

A number of works dealt with the search for an alternative to TNT as the source of free carbon for the formation of DND. In [12], the synthesis of DND through the detonation of aromatic compounds was studied: TATB, HNAB (2,2',4,4',6,6'-hexanitroazabenzene), z-TACOT (tetranitrodibenzotetrazapentalene) and its mixtures with octogen (HMX). It was demonstrated that the yield of DND from the detonation of the considered individual ES is noticeably lower in comparison with TNT−octogen melts, and the most efficient composition for the synthesis is a mixture of z-TACOT/HMX (70 : 30), which provides a noticeable increase in the yield of DND. The mixtures of other compounds with octogen give substantially lower yield in comparison with TNT−octogen melts.

The authors of [13] studied the detonation of DNP (2.4-dinitro-2.4-diazapentane) and its melts with hexogen to reveal differences in the synthesis of DND from aromatic and non-aromatic ES. It was demonstrated that the yield of condensed carbon (CC), DND content in CC and the yield of DND are substantially lower than in the case of TNT.

The source of carbon for the formation of DND during detonation may be not only ES but also organic substances with the negative oxygen balance. For instance, the formation of DND under the conditions of detonation of heterogeneous mixture compositions composed of octogen and a liquid organic additive was studied in [14]. Organic liquids of saturated, unsaturated and aromatic series were used. It was shown that for a number of organic substances the content of DND in CC approaches the corresponding value for TNT−hexogen melts.

Practically all the investigated ES for detonation synthesis are heterogeneous mixtures. The average size of sensitizer particles in them is 150−500 mm. For these essentially nonuniform mixtures, the products of decomposition of the molecules of separate components do not have enough time to get mixed in the zone of chemical reactions to the Chapman-Jouguet point. Estimation of the thickness of the layer in which the diffusion mixing of the products of this decomposition occurs gives a value of ~0.6 mm [2]. A small thickness of the effective diffusion layer in comparison with the usual grain size of a mixed ES allows us to assume that only insignificant mixing occurs during chemical reaction during the decomposition of trotyl/hexogen mixture. The formation of products occurs independently in different micro volumes characterized by different chemical compositions, temperature and perhaps pressure [15]. The effect of octogen dispersity in melts with trotyl on DND yield was studied in [15]. The average size of octogen particles varied within the range 350 to 6 mm. It was shown that a decrease in octogen particle size leads to an increase in

TABLE 1

Physicochemical properties of compounds [19, 20]

ES	ρ_{max}, g/cm^3	T_m, °C	ΔH_m^0, kJ/mol	D, m/s ($\rho_0 = 1.60$)
TNT ($C_7H_5N_3O_6$)	1.64	80.8	21.9	6900
DINA ($C_4H_8N_4O_8$)	1.67	52.5	23.6	7730

Note. ρ_{max} is the maximal density, T_m is melting temperature, ΔH_m^0 is the standard enthalpy of melting, D is detonation velocity.

DND yield from 7.0 to 9.5 %, other conditions being equal. The content of DND in CC (C_{DND}) increases from 50 to 70 %.

Similar results were obtained also in [9] for the melts of trotyl with Avrora. It was demonstrated that an increase in the homogeneity of mixed heterogeneous ES due to a decrease in the size of structural non-uniformities promotes a noticeable increase in the yield of DND. A limiting case is mixing an ES (as a source of carbon) and another ES (as a sensitizing agent) on the molecular level in the form of an ideal solid solution. The only example of DND synthesis from a homogeneous mixture is presented in [10], where the results of experiments for a TNT−TEN (90 : 10) alloy are described. According to the data described in [16], the solubility of TEN in TNT is 13 %, and in this case, not a suspension is formed (as in the case of the melts of TNT with other ES) but a true solution.

In view of the lack of information on the synthesis of DND from homogeneous mixtures, additional studies in this direction are necessary. The homogeneity of compositions may be provided using the mixtures of heterogeneous ES forming liquid eutectic mixtures. It is known that the crystallization of eutectics involves the simultaneous growth of both phases in the liquids of constant composition. Two phases of the eutectics are released in turn, with alternating supersaturation of the liquid with one or another component. In this process, very fine structures of crystal particles are often formed, distinguished by tight packing of the products of solidification of liquid eutectics [17, 18].

In this connection, in the present work, we studied the properties of the melts of trotyl with di(2-nitroxyethyl)-nitramine (DINA). The choice of the latter compounds is due to its low melting point and high mutual solubility of the components. Some physicochemical characteristics of TNT and DINA including their detonation rates are presented in Table 1. One can see that DINA is a more powerful ES, and this factor is important in the detonation synthesis of nanodiamonds.

The goal of the work was to study the synthesis of DND in homogeneous mixtures of two ES − TNT/DINA.

EXPERIMENTAL

Determination of solubility and phase state of the TNT/DINA system

The diagram of state of the binary system TNT/DINA was studied using the method of fusibility, the curves of differential thermal analysis (DTA) were recorded with STA DTG-60 Shimadzu thermoanalyzer (Japan) with the heating rate of 5 °C/min. The modes of melt heating for plotting the fusibility diagram were chosen experimentally taking into account the crystallization of the excess component and eutectics itself.

The dissolution of TNT in DINA was studied by means of refractometry, which is based on the dissolution of the components under study in liquid media, followed by the measurement of refractive index for the solutions of the given concentration at a given temperature. The saturation concentration is determined from the calibration curve. Solubility is determined using a thermostated cell equipped with a magnetic mixer, with control through an optical microscope with the help of the digital refractometer Mettler Toledo RM40 (Switzerland) with a built-in thermostat.

Sample density was determined by means of pycnometry using auto-pycnometer Mikro-Mate 1320 (USA).

Experiments on detonation synthesis

The synthesis of DND was carried out using cylindrical charges 38 mm in diameter, 100 g in mass, which were manufactured by layer-by-layer pouring into the casting form (5−8 layers). For casting, we used both the melts of pure components and TNT/DINA mixtures with TNT content 10−80 %, step 10 %. The features of the behaviour of different melts during casting are to

TABLE 2

Results of experiments on the synthesis of DND from TNT–DINA melts (ρ_0 is charge density)

ES	g_{THT}	ρ_0, g/cm^3	B_{CC}, %	B_{DND}, %	C_{DND}, %
TNT	1.0	1.586	18.91±0.38	2.49±0.36	13.2
TD-80	0.8	1.581	13.70±0.40	2.53±0.32	18.5
TD-70	0.7	1.579	12.86±0.40	4.03±0.31	31.4
TD-60	0.6	1.557	10.77±0.25	3.94±0.20	36.6
TD-50	0.5	1.585	9.05±0.60	3.12±0.33	34.5
TD-40	0.4	1.604	8.30±0.12	4.03±0.15	48.5
TD-30	0.3	1.624	7.05±0.17	2.82±0.42	40.0
TD-20	0.2	1.627	6.12±0.50	2.61±0.20	42.6
TD-10	0.1	1.613	3.97±0.20	1.70±0.19	42.9
DINA	0.0	1.620	3.00±0.08	0.75±0.25	25.0

be stressed. In the case of high trotyl content (above 60 %), a decrease in melt temperature to 64–66 °C causes the release of this component, viscosity increases sharply, and the solution grows turbid. Because of this, charge casting was carried out at somewhat higher temperature. For mixtures with trotyl content 10–40 %, even at 50 °C the melt remains transparent and has low viscosity, so casting was carried out at this temperature. The density of charges was controlled using the hydrostatic method. The charges were blown up in the blast chamber 0.175 m^3 in volume, in the atmosphere of nitrogen with the pressure of 0.8 MPa. The charge was initiated using an intermediate detonator (booster, a tablet of pressed hexogen 20 mm in diameter, with mass of 8 g) and an electric detonator ED-8. The condensed products of the explosion were collected and

sieved through a sieve with mesh size 0.315 mm. The products were analyzed using chemical methods to determine humidity, total carbon content, diamond content and non-combustible admixtures. According to the results of analyses, the yields of condensed carbon (B_{CC}) and diamond (B_{DND}) were calculated in per cent of the mass of ES, and the fraction of the diamond phase in CC (C_{DND}) was calculated as the ratio of diamond mass to the mass of condensed carbon: $C_{DND} = 100B_{DND}/BCC$, %. The obtained values were corrected taking into account the yields of CC and DND from the intermediate detonator. Each experimental point is an average of 2–8 parallel experiments. The results of experiments are presented in Table 2.

RESULTS AND DISCUSSION

The fusibility diagram of TNT/DINA system is shown in Fig. 1. It is typical for systems with unlimited solubility in the liquid state and the absence of any solubility in the solid state, with the temperature of eutectics melting 38 °C (~64 % DINA).

The left part of the liquidus curve characterizes the dependence of TNT solubility in DINA. One can see (see Fig. 1) that within temperature range 55–75 °C TNT solubility in DINA increases monotonously from 42 to 62 %, at the initial region (55–65 °C) the solubility is 42–47 % and substantially increases with temperature rise to 75 °C reaching 62 %.

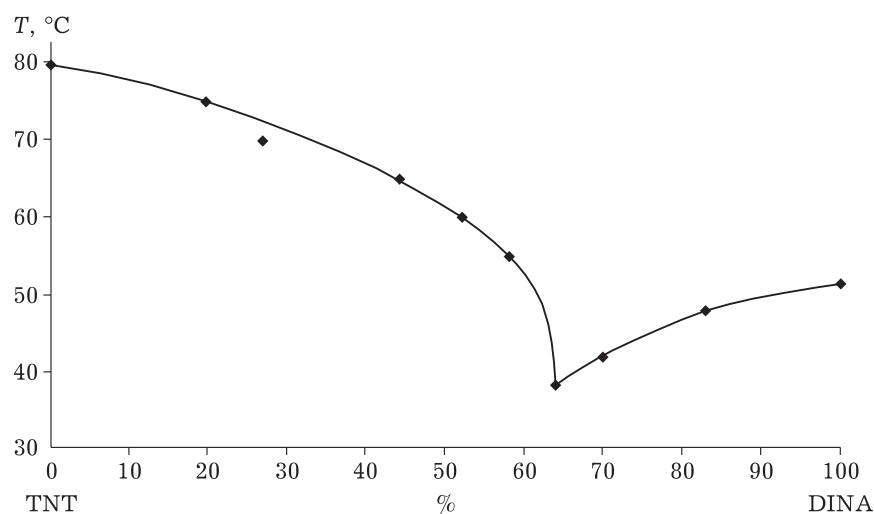The enthalpy of TNT dissolution in DINA (ΔH_d) was determined using Shreder–Le-Chatelier equation [21, 22]:
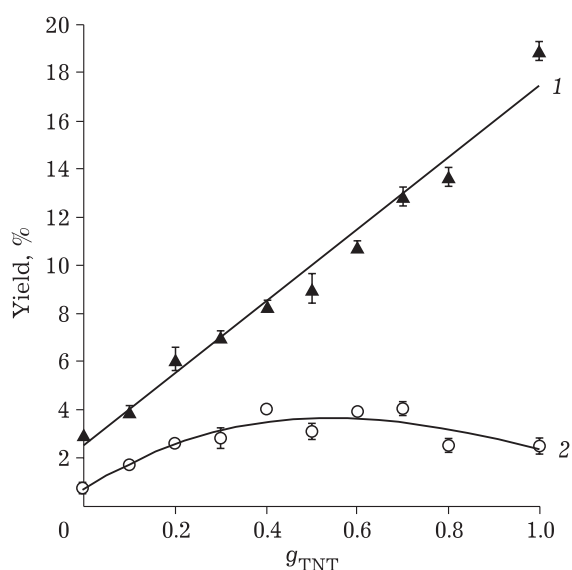

Fig. 1. Fusibility diagram for TNT/DINA system.

Fig. 2. Dependences of the yields of CC (*1*) and DND (*2*) on trotyl content in TNT–DINA melts (horizontal marks show mean-square deviations).

Fig. 3. Dependence of the fraction of DND in CC on trotyl content in TNT–DINA.

$$\ln(N_m) = -\frac{\Delta H_d}{R}\left(\frac{1}{T} - \frac{1}{T_m^{TNT}}\right) \qquad (1)$$

where N_m is the molar concentration of TNT in the saturated solution at a temperature of T; T_m^{TNT} is the melting temperature of pure TNT; R is the universal gas constant.

The enthalpy of TNT dissolution in DINA determined from equation (1) is equal to 29.9 kJ/mol. The obtained results are in agreement with the data reported in [23], where the composition of the eutectic mixture was determined: TNT/DINA = 37 : 63 %.

The enthalpy of TNT dissolution in DINA is substantially higher than the enthalpy of trotyl melting (by 8 kJ/mol), which is the evidence of the interaction between the components in this mixture. The dissolution of TNT in DINA is accompanied by heat absorption and by some increase in volume [24], the density of the system is somewhat lower than the additive value (the calculated additive density is 1.627 g/cm³; experimental density is 1.620 g/cm³).

Analysis of the phase diagram of the two-component system TNT/DINA (see Fig. 1), as well as the data reported in [23], show the possibility to manufacture charges with substantially more homogeneous internal structure than that of the changes with fine powerful ES.

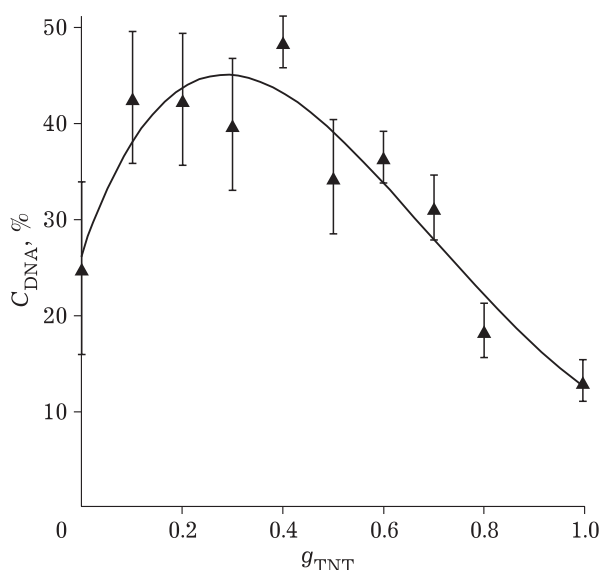The dependences of the yields of CC and DND on the composition of TNT–DINA melts are shown in Fig. 2. The dependence of CC yield on mixture composition is well described by a linear function (correlation coefficient is 0.977):

BCC = $a + bg_{TNT}$

where g_{TNT} is the mass fraction of TNT in the mixture. The coefficients determined by means of the least squares are equal to: $a = 2.50$, $b = 14.94$.

The dependence of DND yield on the composition of TNT–DINA melts has an extremal point. With an increase in TNT content in the mixture to ~40 % the yield of DND reaches a maximum; with a further increase to ~70 % the yield remains practically unchanged at first, and then it decreases and becomes comparable with the yield from pure trotyl.

The dependence of the fraction (C) of DND in CC on the composition of studied melts is shown in Fig. 3. It has a maximum, too. The largest C_{DND} is observed within TNT concentration range 10–40 %. At a higher TNT content and for pure DINA the fraction of DND in CC is noticeably lower.

The results obtained on the yield of DND and its fraction in CC show that from the viewpoint of the synthesis of the nanodiamond carbon phase the most efficient melt is TNT–DINA melt with components ratio close to the eutectics (40/60). It is characterized by the most homogeneous distribution of the components (at the molecular level).

It should be noted that the yield of DND from TNT–DINA melts is much lower than from the melts of trotyl with hexogen and octogen, in which it may exceed 9 % [3, 15]. This is connected with a substantially lower power of DINA in com-

TABLE 3

Calculated and experimental explosive characteristics of trotyl melts with some ES

ES	OB, %	ρ_0, g/cm^3	P, kbar	T, K	C_{DND}, %
TNT−DINA (40 : 60)	−45.6	1.604	224	3603	48.5
TNT−TEN (40 : 60)	−35.7	1.676	249	3750	65.0
TNT−hexogen (40 : 60)	−42.6	1.697	261	3695	67.1
TNT−octogen (40 : 60)	−42.6	1.744	276	3663	67.2

Note. OB is oxygen balance of ES; P, T are pressure and temperature in Chapman-Jouguet point, respectively.

parison with the mentioned ES. Calculated detonation parameters and experimental data on DND content in CC for the mixtures of trotyl with somewhat more powerful ES − sensitizers are presented in Table 3 (TNT content is 40 % in all mixtures). Calculations were carried out using the Bekker−Kistyansky−Wilson equation of state [25] assuming the formation of diamond in products. For diamond, the Cowen equation of state proposed in [26] was used.

The presented data (see Table 3) show that detonation parameters, first of all, detonation pressure, have a determinative effect on the formation of the diamond phase in detonation products. The content of DND in CC increases with an increase in pressure reaching the maximal value at 250−260 kbar and remains practically at this level with further increase in pressure.

CONCLUSION

The processes of TNT dissolution in DINA and the synthesis of DND from this mixture are investigated. The temperature dependence of TNT solubility in DINA within temperature range 55−75 °C and the heat of dissolution are determined. The heat of dissolution is higher by 8 kJ/mol than the heat of trotyl melting, which is the evidence of interaction between the components.

The dependences of the yield of CC and DND on mixture composition were determined. It was revealed that the maximal DND yield is observed in the case of mixtures close to eutectics.

DND content in CC increases with an increase in pressure reaching the maximal value at 260 kbar and remains practically unchanged with further pressure rise.

Acknowledgements

REFERENCES

1 Volkov K. V., Danilenko V. V., Elin V. I. Synthesis of diamond from carbon of ES detonation products, *Fizika Goveniya i Vzryva*. 1990. Vol. 26, No. 3. P. 123−125.

2 Titov V. M., Anisichkin V. F., Malkov I. Yu. Investigation of the syntheiss of ultrafine diamond in detonation waves, *Fizika Goreniya i Vzryva*. 1989. Vol. 25, No. 3. P. 117−126.

3 Kozyrev N. V., Golubeva E. S. Investigation of the synthesis of ultrafine diamonds from a mixutre of trotyl with hexogen, octogen and TEN, *Fizika Goreniya i Vzryva*. 1992. Vol. 28, No. 5. P. 119−123.

4 Xu K., Jin Z., Wei F., Jiang T. Preparation of ultrafine diamonds by explosive detonation method, *Chinese Journal of Energetic Materials*. 1993. Vol. 1, No. 3. P. 19−21.

5 Chen Q., Ma F., Chen P., Yun S., Huang F. Effect of different preservative substances on the formation of condensed carbon in detonation, *Chinese Journal of High Pressure Physics*. 1998. Vol. 12, No. 2. P. 129−133.

6 Liu Y., Wang J., Yu Y. Effect of protective medium on the yield of nanometer diamond, *Chinese Journal of Energetic Materials*. 2005. Vol. 13, No. 5. P. 327−329.

7 Greiner N. R., Phillips D. S., Johnson J. D., Volk F. Diamonds in detonation soot, *Nature*. 1988. Vol. 333, No. 6172. P. 440−442.

8 Forbes J., Davis J., Wong C. Detonation synthesis of nanosize materials, MRS Proceeding. 1996. Vol. 418. P. 439−444.

9 Kozyrev N. V., Sysolyatin S. V., Sakovich G. V. Synthesis of ultrafine diamonds from the melts of trotyl with polycyclic nitramines, *Fizika Goreniya i Vzryva*. 2006. Vol. 42, No. 4. P. 131−134.

10 Kozyrev N. V. Application of radioisotopic tracer technique in the studies of detonation processes, *Fizika Goreniya i Vzryva*. 2008. Vol. 44, No. 6. P. 92−98.

11 Kazutin M. V., Kozyrev N. V., Petrov E. A., Komarova M. V. Synthesis of nanodiamond in the detonation of TNT/CL-20 charges, *Polzunov. Vestn*. 2016. Vol. 1, No. 4. P. 40−44.

12 Anisichkin V. F., Malkov I. Yu., Sagdeev F. A. Synthesis of diamond in the detonation of aromatic nitro compounds. Proc. V All-Union Conference on Detonation. Vol. 1. Krasnoyarsk. 1991. P. 27−30.

13 Pershin S. V., Petrov E. A., Tsaplin D. N. Effect of the structure of ES molecule on the rate of formation and on the properties of ultrafine diamonds, *Fizika Goreniya i Vzryva*. 1994. Vol. 30, No. 2. P. 102−106.

14 Malkov I. Yu. Formation of ultrafine diamond phase of carbon under the conditions of detonation of heterogeneous

mixture compositions, *Fizika Goreniya i Vzryva.* 1991. Vol. 27, No. 5. P. 136−140.

15 Kozyrev N. V., Larionov B. V., Sakovich G. V. Effect of octogen dispersity on the synthesis of nanodiamonds in detonation waves, *Fizika Goreniya i Vzryva.* 2008. Vol. 44, No. 2. P. 79−83.

16 Orlova E. Yu. Chemistry and Technology of Brisant Explosive Substances. Leningrad: Khimiya, 1973.

17 Bochvar A. A. Investigation of the Mechanism and Kinetics of Crystallization of the Melts of Eutectic Type. Moscow-Leningrad: ONTI NKTP SSSR, 1935. 46 p.

18 Ravich G. B., Kuznetsova N. P. *et al.* Phase Equilibria and Physical Properties of Polynitrocompounds (Microphase Analysis). Moscow: Mashinostroenie, 1969. 82 p.

19 Meyer R., Kohler J., Horburg A. Explosives. 6 ed. Wiley-VCH, 2007.

20 US Pat. No. 2461582, 1949.

21 Karapetyants M. Kh. Chemical Thermodynamics. Moscow: Khimiya, 1975.

22 Anosov V. Ya., Ozerova M. I., Fialkov Yu. Ya. Foundations of Physicochemical Analysis. Moscow: Nauka, 1976.

23 Kozak G. D., Kondrikov B. N., Lin Z. Detonation of TNT−DINA and DNT−PETN Cast Charges, 31st Int. Annual Conference of ICT. Karlsruhe, Germany, 2000. P. 78.

24 Moelwyn-Hughes E. A. Physical Chemistry. L.−NY−Paris: Pergamon Press, 1961.

25 Kozyrev N. V. Reparametrization of the BKW equation of state for CHNO explosives which release no condensed carbon upon detonation, *Central European Journal of Energetic Materials.* 2015. Vol. 12, No. 4. P. 651−669.

26 Gubin S. A., Odintsov V. V., Pepekin V. I., Sergeev S. S. Effect of shape and size of diamond and graphite crystals on the phase equilibrium of carbon and detonation parameters, *Khim. Fizika.* 1990. Vol. 9, No. 3. P. 401−417.