

Unconventional emulsion explosives with low detonation velocities

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Abstract: Detonation velocities of unconventional emulsion explosives containing epispastic polystyrene (EPS) micro-balloons were studied experimentally and theoretically. Fine-particle lithium and zinc oxides have been prepared by the detonation of emulsion explosives of the metal nitrates, $M(NO_3)_x$ ($M = Li, Zn$) as oxidizers and paraffin as fuels, at low velocity. For the calculations in which the first set of decomposition products is assumed, predicted heats of detonation of emulsion explosives with the product H_2O in the gas phase have a deviation of 586 kJ/kg from results with the product H_2O in the liquid state. The results obtained enable a comparison of the usefulness of both calculating and measuring methods. The influence of lithium and zinc nitrates contained in the emulsion matrix on the detonation velocities of the explosives was discussed.

Keywords: Emulsion explosives, EPS micro-balloons, nitrates of metals, detonation velocity

1 Introduction

A zinc and lithium composite oxide is the subject of growing interest for different applications in electronic components [1-4]. Especially, G.Ceder regarded that $LiZnO_2$ compound has a higher voltage than that of $LiCoO_2$ [5]. More recently, it was reported that these oxides nanomaterials have generated tremendous interests in both the scientific and engineering community, which has visibly led to rapid and intense growth in research focus [6-13].

Emulsion explosives belong to commercial explosives. They were developed in the early 1960s [14, 15] and have become quite important blasting means because of their comparatively high detonation parameters and exceptionally good safety characteristics. Emulsion explosives were prepared by agitation of a supersaturated aqueous solution of some oxidizers and a fuel doped with an emulsifying agent [16]. A distinguishing feature of emulsion explosives is that in the aqueous solution, the oxidizer is present in the form of tiny droplets covered with a very thin fuel layer. Consequently, the interfacial surface of the emulsions is very large, as a result of which their detonation behavior is almost ideal, unlike other ammonium nitrate based composite fuels. In the work described here, we studied the detonation velocities of emulsion explosives containing EPS micro-balloons. The emulsion matrix was prepared using aqueous solutions of ammonium nitrate, lithium nitrate and zinc nitrate. The contents of other ingredients were changed insignificantly in order to maintain the oxygen balance. For each explosive, the detonation velocity was measured and calculated. The results obtained enabled a comparison of the efficiency of both methods for discussing the phenomenon of low detonation velocity of the unconventional emulsion explosives. They were also used to analyze the effect of metal nitrates and EPS on the low detonation velocity of the explosives and to choose the formulations characterized by the low detonation velocities.

2 Experiments

The composition thus prepared is extremely insensitive to initiation, and, hence, it has to be sensitized by appropriate additives (EPS micro-balloons). The basic oxidizer used in emulsion explosives is ammonium nitrate; lithium nitrate and zinc nitrate are added to synthesize nanometer particles of composite oxides. The fuel phase consists of mineral oils and paraffin.

The explosive charges were put into a thin plastic bag with an approximate 666, 863, and 1149 kg/m^3 density respectively. For each charge an electric No.8 initiator was used. The detonation experiments were performed in an explosive chamber (showed in Figure 1). This method provides a very fast

quenching space. The air surrounding the charge provides efficient cooling of detonation products and thus reduces the reuniting of obtained nanoparticles. The detonation experiments were done in a steel tank. The explosive charge was placed in a polyethylene bag, which was suspended at the tank centre. The detonation products contained some impurities such as fragments from the tank walls (Fe_2O_3 , Al_2O_3), copper and steel from the detonator, and PE from the bag and the leg wires of the detonator. The compositions of the emulsion matrices are given in the latter reaction formula. The emulsions were prepared using a simple facility consisting of a thermostat and a container equipped with a stirrer. The solution of oxidizers was heated to 110°C and then slowly added to the container, in which a preheated (90°C) mixture of fuels (oil and paraffin) with the emulsifier was agitated with the stirrer at a speed of 800 rpm. After adding the entire amount of the oxidizer, the agitation was continued for about three minutes to obtain fine particles of the emulsion. The final explosive mixtures were prepared by mixing the emulsion matrices with EPS micro-spheres (mean size 1.5mm). Mixing was performed carefully until the distribution of the micro-spheres in the emulsion matrix became uniform. In all experiments, the mass fraction of micro-spheres was 1%, 3%, and 3% respectively (above 100%). The initial density of the explosives was determined from the weight and volume of samples in plastic tubes used in detonation velocity measurements. The detonation velocity was measured by ionization sensors. The explosive charges were confined in plastic tubes 250 mm long with an inner diameter of 32 mm. In each charge there were measuring courses 50 mm long, and the first sensor was at 90 mm from the booster. These values were large enough to ensure a steady detonation and determination of the detonation velocity with an accuracy of about 1%.

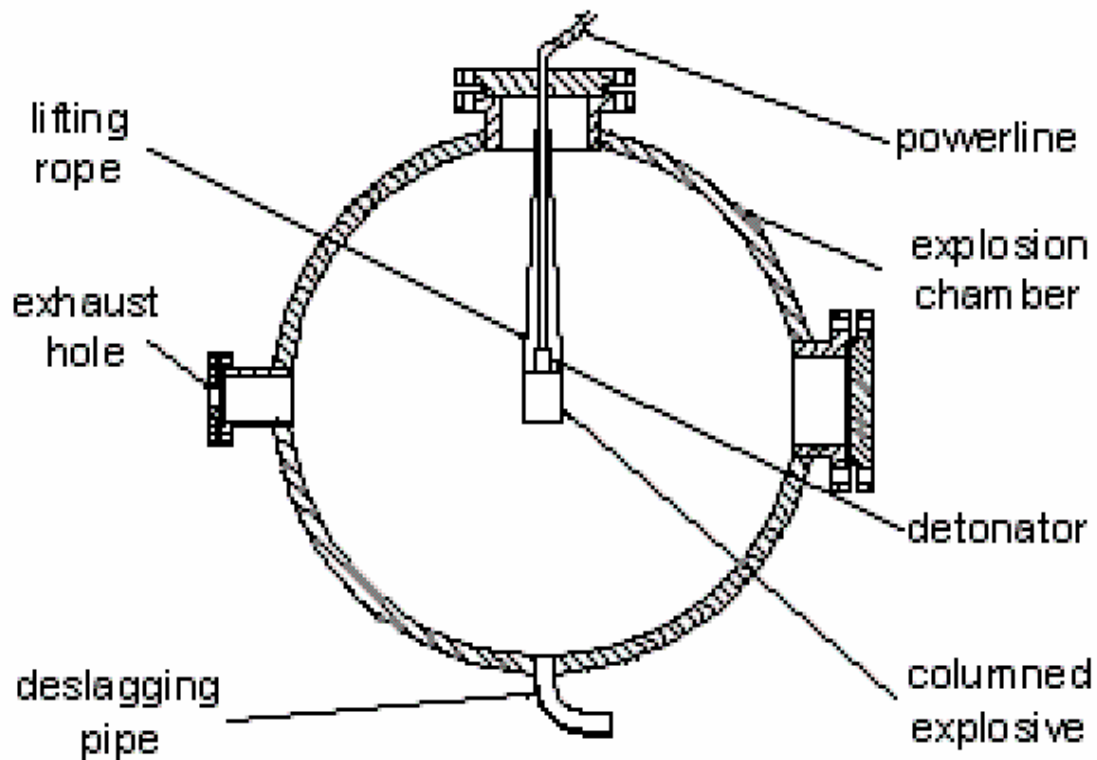


Figure 1. Schematic of explosion chamber

3 Velocity Calculations

A method of estimating D at ρ invokes the thermochemical properties[17]. Their empirical relationships are as follows.

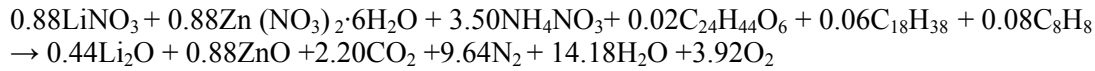
$$\phi = NM^{1/2}Q^{1/2}, \quad (1)$$

$$D = 1.01\phi^{1/2}(1 + 1.3\rho_0), \quad (2)$$

Where, N is moles of gaseous detonation products per g of water-gel explosive (mol gas/g water-gel explosive);

M is average molecular weight of detonation product gas (g gas/mol gas); and

Q is chemical energy of detonation reaction (cal/g).



Heats of formation (kJ/mol)

Li_2O , -595.80; ZnO , -350.06; H_2O (liq), -285.80; LiNO_3 , -482.20; $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, -2306.60;

NH_4NO_3 , -365.60 [18].

$\text{C}_{24}\text{H}_{44}\text{O}_6$, -2135.21 kJ/mo; $\text{C}_{18}\text{H}_{38}$, -186.62 kJ/mol; C_8H_8 , 220.17 kJ/mol [19].

H_2O (gas), -242.00; CO_2 , -393.70 [20].

If we consider the water of detonation products in liquid state,

$$Q = 0.44 \times (-595.80) + 0.88 \times (-350.06) + 2.20 \times (-393.70) + 14.18 \times (-285.80) - 0.88 \times (-482.20) - \\ 0.88 \times (-2306.60) - 3.50 \times (-365.60) - 0.02 \times (-2135.21) - 0.06 \times (-186.62) - 0.08 \times (220.17) \\ = -262.15 - 308.05 - 866.14 - 4052.64 + 424.34 + 2029.81 + 1279.60 + 42.70 + 11.20 + 17.61 \\ = -1683.72 \text{ kJ/kg}_o$$

$$Q_p [\text{H}_2\text{O} (\text{l})] = -Q [\text{H}_2\text{O} (\text{l})] \times 1\text{kg} = 1683.72 \text{ kJ}$$

$$Q_v [\text{H}_2\text{O} (\text{l})] = 1683.72 \text{ kJ} + (2.20 + 9.64 + 3.92) \times 8.314 \times 10^{-3} \times 298.15 \text{ kJ} \\ = 1722.79 \text{ kJ}$$

If we consider the water of detonation products in vapor state,

$$Q [\text{H}_2\text{O} (\text{g})] = -1683.72 + 14.18 \times (-242.00 - (-285.80)) = -1683.72 + 621.08 \\ = -1062.64 \text{ (kJ/kg)}.$$

$$Q_p [\text{H}_2\text{O} (\text{g})] = -Q [\text{H}_2\text{O} (\text{g})] \times 1\text{kg} \\ = 1062.64 \text{ kJ}$$

$$Q_v [\text{H}_2\text{O} (\text{g})] = 1062.64 \text{ kJ} + (2.20 + 9.64 + 14.18 + 3.92) \times 8.314 \times 10^{-3} \times 298.15 \text{ kJ} \\ = 1136.86 \text{ kJ}$$

If we consider the water of detonation products in liquid state,

$$N = (2.20 + 9.64 + 3.92)/1000 = 15.76/1000 = 0.01576 \text{ (mol/g)}$$

$$M = (2.20 \times 44 + 9.64 \times 28 + 3.92 \times 32)/15.76 = (96.80 + 269.92 + 125.44)/15.76 \\ = 31.23 \text{ (g/mol)}$$

$$Q = Q_v [\text{H}_2\text{O} (\text{l})] / 4.18 = 1722.79 / 4.18 = 412.15 \text{ (cal/g)}$$

$$\phi = 0.01576 \times 31.23^{1/2} \times 412.15^{1/2} = 0.01576 \times 5.59 \times 20.30 = 1.788$$

When $\rho = 1149 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 1.788^{1/2} (1 + 1.3 \times 1.149) = 1.01 \times 1.337 \times 2.49 = 3.38 \text{ (Km/s)}$$

When $\rho = 863 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 1.788^{1/2} (1 + 1.3 \times 0.863) = 1.01 \times 1.337 \times 2.12 = 2.87 \text{ (Km/s)}$$

When $\rho = 666 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 1.788^{1/2} (1 + 1.3 \times 0.666) = 1.01 \times 1.337 \times 1.87 = 2.52 \text{ (Km/s)}$$

If we consider the water of detonation products in vapor state,

$$N = (2.20 + 9.64 + 14.18 + 3.92)/1000 = 29.94/1000 = 0.02994 \text{ (mol/g)}$$

$$M = (2.20 \times 44 + 9.64 \times 28 + 14.18 \times 18 + 3.92 \times 32)/29.94$$

$$= (96.80 + 269.92 + 255.24 + 125.44)/29.94 = 24.96 \text{ (g/mol)}$$

$$Q = Q_v [\text{H}_2\text{O (g)}]/4.18 = 1136.86 / 4.18 = 271.98 \text{ (cal/g)}$$

$$\phi = 0.02994 \times 24.96^{1/2} \times 271.98^{1/2} = 0.02994 \times 5.00 \times 16.49 = 2.469$$

When $\rho = 1149 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 2.469^{1/2} (1 + 1.3 \times 1.149) = 1.01 \times 1.571 \times 2.49 = 3.95 \text{ (Km/s)}$$

When $\rho = 863 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 2.469^{1/2} (1 + 1.3 \times 0.863) = 1.01 \times 1.571 \times 2.12 = 3.36 \text{ (Km/s)}$$

When $\rho = 666 \text{ kg.m}^{-3}$,

$$D = 1.01 \times 2.469^{1/2} (1 + 1.3 \times 0.666) = 1.01 \times 1.571 \times 1.87 = 2.97 \text{ (Km/s)}$$

The experimental results are as follows.

When $\rho = 1149 \text{ kg.m}^{-3}$, $D_1 = 1397$, $D_2 = 1481$, $D_a = 1439 \text{ (m/s)}$.

When $\rho = 863 \text{ kg.m}^{-3}$, $D_1 = 1511$, $D_2 = 1541$, $D_a = 1526 \text{ (m/s)}$.

When $\rho = 666 \text{ kg.m}^{-3}$, $D_1 = 1703$, $D_2 = 1687$, $D_a = 1695 \text{ (m/s)}$.

4 Results and Discussion

Clearly, the predicted heats and velocities of detonation for State Equation the new emulsion explosive are reasonable. Many of the reported values of the heats of detonation of the explosives described herein indicate that the experiments were analysed assuming the H_2O as being in either the vapour or liquid state. Those results in which H_2O is assumed to be in the vapour state are typically denoted $Q [\text{H}_2\text{O (g)}]$, whereas the results in which H_2O is assumed to be in the liquid state is denoted as $Q [\text{H}_2\text{O (l)}]$. In order to compare our results against these, we have also used the Dulong-Petit's values of the specific heat for liquid phase H_2O in order to compare with those results in which the product H_2O is assumed to be in the close-grained state. Heats of detonation were calculated using the explosive reaction formula in which the Chapman–Jouget (C–J) state is calculated for the designated explosive. In these calculations, the heat of detonation corresponds to the energy difference between the reactants and all products at the end of this expansion. It is concluded that the calculated results are more than ones of measuring experiments of detonation velocity over a range of initial densities.

A typical example of this is seen in Figure 2, which shows data from our experiments. The data of Figure 2 show how the introduction of metal nitrates and EPS into the emulsion matrices affects the detonation velocities. From the results presented in the figure it follows that the use of lithium nitrate and zinc nitrate as two additional oxidizers deteriorates the parameters considered most insignificantly, whereas the addition of EPS to the mixture gives an explosive with comparatively low detonation parameters but its value is rather poor with the increment of the content of EPS. The absence of correlation between the relative detonation velocity and the parameter density indicates that there are other factors influencing these characteristics. One of these can stem from the fact that the relative detonation velocity was measured for different samples and under different conditions. Therefore, we conducted detonation velocity tests to determine the performance of the explosive using initial densities of the unconventional emulsion explosives. Here the values of D_{exp} are much smaller than those calculated. This indicates that in detonation velocity tests, more ammonium nitrate reacts in the

detonation wave and there is better agreement between measured and theoretical detonation velocities. A comparison of the data between calculating and measuring shows that the content of EPS has a strong effect on detonation velocities, which is manifested in nonideal detonation properties.

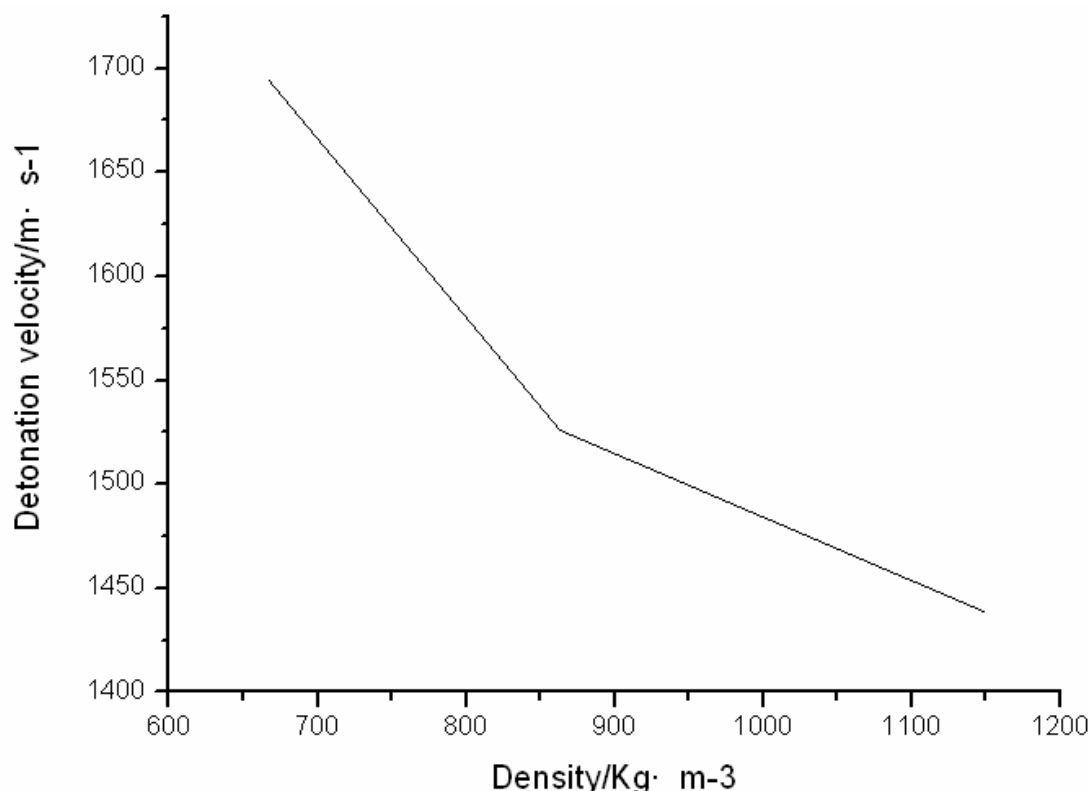


Figure 2. Detonation velocity of unconventional emulsion explosive over a range of initial densities.

5 Concluding remarks

In the final analysis, we discuss detonation velocities of the unconventional emulsion explosives for synthesis of lithium and zinc oxides, which we believe, has never been reported. We can grow these nanoscale structures in a cheap manner through the addition of nitrates using the emulsion explosive detonation process [21]. This novel method allows us to synthesize nanometer composite oxide powders.

The results of the experiments described here show that the detonation velocity test can be used with advantage for quantitative determination of explosive performance. Results of these experiments together with data of calculation formula of the process allow one to obtain the equation of state for detonation products and, hence, to estimate their detonation velocity. The addition of metal nitrates to emulsion compositions deteriorates the detonation properties of explosives containing only ammonium nitrate, which is manifested in a decrease in detonation velocities. The decrease in performance is most considerable in the initial stage of expansion of detonation products. With increase in the volume of EPS, these discrepancies decrease. This implies that chemical reactions also proceed in expanding detonation products and additional energy released in these reactions is converted to mechanical work. For this reason, detonation velocities determined in the initial stage of expansion depend strongly on the content of EPS micro-balloons.

Acknowledgements

The authors are grateful to The Anhui Province Education Office for supporting this work.

References

- [1] N. V. Borissova, M. M. Pivovarov, V. M. Ushakov, and M. M. Schultz, Enthalpies of formation of vitreous and crystalline pyrophosphates of (lithium oxide or sodium oxide + zinc oxide + phosphorus pentoxide)[J]. *J. Chem. Thermodynamics*, 1996, 28(2), pp. 115-124
- [2] Carl Johan Rydh, Björn A. Sandén, Energy analysis of batteries in photovoltaic systems. Part I: Performance and energy requirements[J]. *Energy Conversion and Management*, 2005, 46(11-12), pp. 1957-1979
- [3] T. R. Jensen, R. G. Hazell, A. Nørlund Christensen, and J. C. Hanson, Hydrothermal Synthesis of Lithium Zinc Phosphates: Structural Investigation of Twinned α -Li₄Zn (PO₄)₂ and a High Temperature Polymorph β -Li₄Zn (PO₄)₂[J]. *Journal of Solid State Chemistry*, 2002, 166(2), pp. 341-351
- [4] Alexander Apelblat and Eli Korin, The vapour pressure of water over saturated solutions of sodium sulfate, calcium bromide, ferric chloride, zinc nitrate, calcium nitrate, and lithium nitrate at temperatures from 278.15K to 323.15K[J]. *J. Chem. Thermodynamics*, 2002, 34(10), pp. 1621-1637
- [5] G. Ceder, M.K.Aydinol, A.F.Kohan, Application of first-principles calculations to the design of rechargeable Li-batteries[J]. *Computational Materials Science*, 1997, 8(1-2), pp. 161-169
- [6] Yongjun He, Preparation of polyaniline/nano-ZnO composites via a novel Pickering emulsion route[J]. *Powder Technology*, 2004, 147(1-3), pp. 59-63
- [7] Jun Wang, Jieming Cao, Baoqing Fang, Peng Lu, Shaogao Deng, Haiyan Wang, Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids[J]. *Materials Letters*, 2005, 59(11), pp. 1405-1408
- [8] Qinyi Zhang, Changsheng Xie, Shunping Zhang, Aihua Wang, Bailin Zhu, Lin Wang, Zhongbao Yang. Identification and pattern recognition analysis of Chinese liquors by doped nano ZnO gas sensor array[J]. *Sensors and Actuators B*, 2005, 110(2), pp. 370-376
- [9] Ting Fang, Jenqong Duh, and Shyangroeng Sheen, LiCoO₂ cathode material coated with nano-crystallized ZnO for Li-ion batteries[J]. *Thin Solid Films*, 2004, 469-470, pp. 361-365
- [10] Chyiching Hwang, Tsungyung Wu, Jun Wan, Jihsheng Tsai, Development of a novel combustion synthesis method for synthesizing of ceramic oxide powders[J]. *Materials Science and Engineering B*, 2004, 111(1), pp. 49-56
- [11] Jun Zhang, Yongdong Yang, Baolong Xu, Feihong Jiang, Jianping Li, Shape-controlled synthesis of ZnO nano- and micro-structures[J]. *Journal of Crystal Growth*, 2005, 280(3-4), pp. 509-515
- [12] Huihu Wang, Changsheng Xie, Dawen Zeng, Controlled growth of ZnO by adding H₂O[J]. *Journal of Crystal Growth*, 2005, 277(1-4), pp. 372-377
- [13] Pu Xian Gao, Chang Shi Lao, William L. Hughes, Zhong L. Wang, Three-dimensional interconnected nanowire networks of ZnO[J]. *Chemical Physics Letters*, 2005, 408(1-3), pp. 174-178
- [14] R. S. Egly and A. E. Neckar, Water resistant sensitizers for blasting agents, U.S. Patent, 1964, No. 3,161,551
- [15] N. E. Gehrig, Aqueous emulsified ammonium nitrate blasting compositions containing nitric acid, US Patent, 1965, No. 3,164,503
- [16] S. Cudzilo, P. Kohlicek, V. A. Trzcinski, and S. Zeman. Performance of Emulsion Explosives. *Combustion, Explosion, and Shock Waves*, 2002, 38(4), pp. 463-469
- [17] Jonas A. Zukas, William P. Walters. Explosive effects and applications. New York: Springer-Verlag New York, Inc., 1998, pp.124
- [18] Ye Dalun, Hu Jianhua. Practical handbook of energetics data for inorganic compounds (second edition). Beijing: Metallurgical industry press, 2002, pp. 533-594
- [19] Bao Jingdan. Applied thermal chemistry. Shanghai: East China Institute of Chemical Engineering Press, 1989, pp. 94
- [20] Jacqueline Akhavan. The Chemistry of Explosives. Cambridge: The Royal Society of Chemistry, 1998, pp. 103
- [21] Li Xiaojie, Xie Xinghua, Li Ruiyong. Detonation synthesis for nano-metallic oxide powders. *Explosion and Shock Waves*, 2005, 25(3), pp. 271-275