DETONATION AND DEFLAGRATION PROPERTIES OF PYROTECHNIC MIXTURES

KATSUMI TANAKA
National Institute of Materials and Chemical Research,
Tsukuba Research Center, Tsukuba, Ibaraki 305, Japan, tanaka@nimc.go.jp

ABSTRACT

Theroretical calculation of detonation and deflagration properties of pyrotechnic mixtures have been performed including report charges and display charges. Calculation were performed with the KHT (Kihara-Hikta-Tanaka) code[1]. KHT results are compared with a modified version of the TIGER code[2] which allows calculation with 900 gaseous and 600 condensed product species at high pressure. Detonation properties computed by KHT and BKWS (Becker-Kistiakowskii-Wilson) give favorable agreement with experimental results of detonation velocity measurements. Hydrodynamic computation by one dimensional Lagrangian hydrodynamic code using the isentrope given by KHT constant volume explosion, indicated that experimental results for blast wave measurement for 30kg and 50kg of report charge were an incomplete reaction. Underwater detonation experiments with explosive charge of 25g, however, indicates a more energetic nature than the KHT prediction. This scale effect indicates complicated slow reactions and a number of condensed phase deflagration products of powder mixtures such as aluminum or titanium with oxidizers such as potassium perchlorate or nitrate salts as suggested by Hobbs et al[3].

INTRODUCTION

The study of explosion properties of pyrotechnic mixtures have been used to obtain the safety separation distance between manufacturing plants and inhabited residence. A recent accident which occurred in unapproved buildings of a fireworks company in Japan showed unexpected, large damages to surrounding buildings. Several experiments have been performed for report charges to study the detonation or deflagration properties of firework mixtures.

DETONATION/DEFLAGRATION PROPAGATION

Detonability of report charges and display charges have been studied by two steel tube tests. One is a 50/60 mm steel tube test based on the method of TRANSPORTATION OF DANGEROUS GOODS/TEST AND CRITERIA recommended by the UN. Another is a 30/34 mm steel tube test with a steel witness plate to measure the plate dent and confirm the detonation propagation. A report charge of Al/Ti/KP(potassium perchlorate) (15/15/70 weight percent) powder mixtures of initial density of 0.9 g/cm3 gives a dent of approximately 0.5 mm in depth but no dent was observed with the display charge. Detonation velocity has been measured by resitance wire to continuous change of electrical resitance or two contact pins. Both tests have shown the detonation propagation velocity of 1000 to 2000 m/s. The average detonation velocity was approximately 1500m/s. A high epxlosive booster charge of 50 g was used for the UN classification test for the CLASS 1 substances. A pentolite charge of 20 g or electric fuse was used for the 30/34 mm steel tube test to initiate a sample. The continuous detonation velocity measurements have suggested unsteady detonation propagation.

Mat. Res. Soc. Symp. Proc. Vol. 418 © 1996 Materials Research Society

Table 1A Assumed detonation products to KHT calculation:
KCl,O2,Cl2,AlCl3,SO2,SO,S,KCl(s),Al(s),Al2O3(s)

	D(m/s)	P(GPa)	T(K)	Qd(J/g)	Qis(J/g)
KP/Al/S;10/3/1	2054(1800)	1.12	6410	7218	
KC/Al/S;10/3/1	1753(1700)	1.82	6463	7399	
KC/Al;90/10	2398	1.33	3528	3386	1548
KC/Al;85/15	2288	1.22	4641	4926	1674
KC/Al;80/20	2004	0.94	5635	6462	1477
KC/Al;75/25	1507	0.52	6526	7998	925
KC/Al;70/30	fail				

Table 1B
KCl,O2,Cl2,AlCl3,SO2,SO,S,Al,AlO,Al2O,Al2O3(s)

	D(m/s)	P(GPa)	T(K)	Qd(J/g)	Qis(J/g)
KP/Al/S;10/3/1	2427(1800)	1.95	7132	6508	
KC/Al/S;10/3/1	3452(1700)	1.75	7341	6554	
KC/Al;90/10	3369	2.75	3528	3386	1603
KC/Al;80/20	2994	2.93	5635	6462	3214
KC/Al;75/25	2565	0.52	6526	7998	3394
KC/Al;70/30	2565	1.80	8192	8270	3478
KC/Al;65/35	2776	1.33	3528	7144	3373
KC/Al;60/40	2957	1.22	4641	5666	3285
KC/Al;50/50	2938	0.94	5635	2704	2143
KC/Al;40/60	fail				

Table 1C
KCl,K2CL2,O2,Cl2,AlCl3,SO2,SO,S,Al,AlO,Al2O,Al(s),Al2O3(s)

	D(m/s)	P(GPa)	T(K)	Qd(J/g)	Qis(J/g)
KP/Al/S;10/3/1	2222(1800)	1.25	7147	6625	2967
KC/Al/S;10/3/1	2044(1700)	1.47	7353	6683	2750
KC/Al;90/10	2548	1.89	3486	2419	1783
KC/Al;80/20	2496	2.01	6351	5503	3193
KC/Al;75/25	2247	1.68	7459	7068	3407
KC/Al;70/30	1874	1.21	8397	8538	3511
KC/Al;65/35	2155	1.56	7638	7500	3398
KC/Al;60/40	2393	1.86	6557	6005	3289
KC/Al;50/50	2465	1.83	3979	3047	2172
KC/Al;40/60	fail				

KP(Potassium Pechlorate);KClO4, KC(Potassium Chlorate);KClO3
();measured by Hatanaka et al[4]. D; Detonation velocity
P; Chapman Jouguet pressure Qd: Heat of detonation for C-J composition
Qis; Blast wave energy(TNT 4520 J/g)

Hobbs and author[3] studied the equilibrium calculations of firework mixtures using BKWS-TIGER which can reproduce approximately the detonation velocity of report charges composed of aluminum, titanium and potassium perchlorate(KP) where the major component of detonation products are Al2O3(l), Ti3O5(l), KCl(l) for condensed phase and O2,O,KCl,KO,TiO2, AlO and ClO for gaseous products. A large number of possible detonation products and phase changes of condensed products for report charges and display charges makes equilibrium calculations difficult. Phase changes under high pressure state are still unknown. In the Chapman Jouguet calculations by KHT, 14 species of detonation products were assumed as shown in Table 1. In Table 1A, formation of solid KCl was assumed. Tables 1B and IC assume no condensed phase KCl. The detonation temperatures of report charges and display charges are well higher than boiling point of KCl under normal condition. The assumption of K2Cl2 as a product reproduce the detonation velocity measurements. Tiger-BKWS also reproduces detonation properties of report charges for the oxygen-rich mixtures. However, Tiger-BKWS calculation which assumes the chemical equilibrium state could not predict the explosive hazard for fuel-rich explosives, where the major detonation products predicted by BKWS are in condensed phase for pyrotechnic mixtures. Then total quantity of predicted gaseous species are negligibly small for fuel(metals)-rich pyrotechnic mixtures. The explosive hazards for fuel-rich pyrotechnic mixtures should be in non-chemical equilibrium state. The experimental and calculated detonation properties of the pyrotechnic mixtures are similar to the gaseous detonation. Little change of detonation velocities was predicted with the variation of initial densities by both KHT and BKWS.

BLAST WAVE MEASUREMENTS

Field experiments[5] of blast waves for typical report charge for titanium, aluminum and potassium perchlorate(Al/Ti/KP 15/15/70 weight percent) showed the TNT equivalence of about 50 % for a charge weight of 30 and 50kg. Also, blast wave properties of H-6 (RDX/TNT/Al/Wax 45/30/20/5) high explosive charge of 100kg was measured. The report charge was confined in a cardbord drum and initiated by electric squib. The pressure of blast wave was measured by piezo-electric transducers at several locations. Measured blast wave profile for aluminum loaded explosives of H-6 compares well with numerical calculation by the OBUQ code, which is a one dimensional Lagrangian hydrodynamic code for blast waves and undewater detonations. The used equations of state of detonation products are calculated by KHT code where the isentropes through the chapman-Jouguet point are assumed. The report charges tested give lower overpressure than numerical calculation. This result indicates that the several tens microns of aluminum of particle size included in report charges reacted partially. Case given in Table1A predicts lower overpressure. The time of arrival of the shock wave are shown in Fig.1 and Fig.2 for measurements and calculation. For the case of H-6, the difference of arrival time is considered to be an 3 to 5 ms initiation delay by commercial electric detonators. However, for the case of report charges, the difference of time arrival between calculation and experimetal measurement is approximately 20 ms. This indicates a slow deflagration propagation rate. Experimental results show the increase of TNT equivalence at far distance indicating successive reaction behind the shock wave.

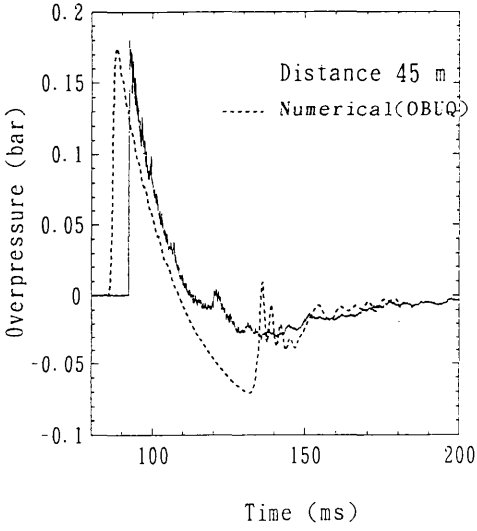

Fig.1 Blast waves of H-6 100 kg

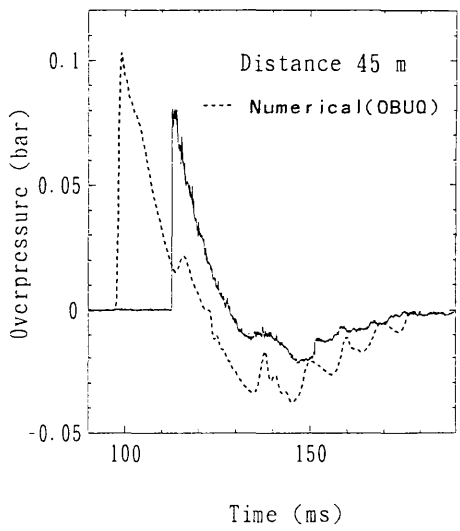

Fig..2 Blast waves of report chrage

UNDERWATER EXPLOSION

The underwater detonation for the Al/Ti/KP(15/15/70 weight percent) system showed a bubble energy of 2 to 2.5 kJ/g compared to the 1.85 kJ/g of TNT. The bubble energy represents the expansion work by explosion products for underwater explosion. Shock energy of this report charge was 0.35 to 0.39 kJ/g comparing with 0.84 to 0.88 kJ/g for TNT. The underwater detonation tests showed the bubble energy of energy measurement of 3 to 3.5 kJ/g for Al/potassium chlorate(KC) which is nearly twice of bubble energy of TNT. Hydrodynamic calculation by OBUQ gives lower explosion energy than experimental results. Bubble energy was estimatd by both bubble pulse of oscillation time and maximum bubble radius. Both estimations give an agreement within a few percent of an experimental error which indicates the instantaneous reaction of report charges. Explosion energies of Al/KC report charges were measured as a function of aluminum content by Aoti et al[6]. In the Al/KC system, 50 wt.% of atomized aluminum gives maximum bubble energy. A display charge composed of KP/barium nitrate/Al/sulfur(38/8/46/8 weight percent), which has no detonability, also showed a bubble energy of 3 to 3.5 kJ/g, this was estimated by bubble pulse duration and a shock energy of 0.16 to 0.18kJ/g. KHT and BKWS cannot predict these extremely large energy of deflagaration products.

DISUCUSSION

A most of heat of reaction is generated by solid or liquid alumina which gives high reaction energy and consumes most of oxygen of report charges and display charges. Thus, the total amount of gaseous products are small and reduce the detonation/deflagaration preesure.

Then the blaswave effects for pyrochnic mixtures with high reacion energy are relatively low due to the less work than TNT energy performed by an expansion of gaseous products which is main energy of blast waves and underwater detonation. The several thousands Kelvin of detonation or deflagration temperature makes many species vaporize. Experiments using small charges show nearly complete reaction, while large scale experiments indicate incomplete reaction. Blast wave for 30 to 50 kg of weakly confined report charges were measured within 200 ms, while the energy of small scale experiments for 25 g of report charges were measured within 100 ms. An extraordinary long duration of bubble pulse observed in display charges can be considered a result of slow reaction. However, the large bubble energy observed in small scale underwater experiments of report charges is still unknown. Observed bubble energy corresponds to nearly the total energy of chemical reaction. The measurement of reaction products will give the solution of the mechanism of high blast performance. The reaction of water and deflagration products is under the consideration in underwater explosion. Also, the effect of heat transfer into water from a bubble should be considered in future work.

CONCLUSION

The detonation and deflagration properties of report charges and display charges are studied. The high reaction temperature makes most of products vaporize, except aluminum oxide, which gives high blast wave effects. An increase of TNT equivalence at far distance for blast wave experiments of the KP/Ti/Al pyrotechnic mixtures suggests the continuous reaction after explosion.

REFERENCE

1. K.Tanaka,"Detonation Properties of High Explosives Calculated by Revised Kihara-Hikita Equation of State,"Proceedings Eighth Symposium(International) on Detonation, Albuquerque, 548,NM(1985)

2. M.L.Hobbs and M.R.Baer,"Calibrating the BKW-EOS with a Large product Species Data Base and Measured C-J Properties," Tenth Symposium(International) on Detonation, Boston,MA(1993)

3. M.L.Hobbs, K.Tanaka, T.Matsunaga and M.Iida, "Equilibrium Calculations of Firework Mixtures," 3rd(Beijing) International Symposium on Pyrotechnics and Explosives, Beijing China(1995)

4. S.Hatanaka,A.Miyahara,T.Hayakawa and Y.Hirosaki,"Steel Tube Test for Pyrotechnic Mixtures,"Japan Explosive Society Spring Symposium,Tokyo,Japan(1994)

5.M.Iida,Y.Nakayama,T.Matsunaga,S.Usuba,Y.Kakudate,M.Yoshida,K.Tanaka and S.Fujiwra, J.National Chemical Laboratory for Industry 85,No.6, 193(1990)

6. T.Aoti,A.Miyake and T.Ogawa, National University of Yokohama, private communication