Research paper

Reaction wave propagation phenomena of tri−n−butyl phosphate and fuming nitric acid (TBP/FNA) mixture by shock loading

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Abstract

In this article, the results of measuring the reaction wave propagation velocities of a tri−n−butyl phosphate (TBP) and fuming nitric acid (FNA) mixture by optical and electrical methods are reported, in order to examine the difference in the reaction by incident shock pressure. The TBP/FNA mixture was found to explode by different mechanisms with the strength of incident shock pressure. That is, under strong incident shock pressure, the reaction propagates in the state of C−J detonation from the beginning, and under weak incident shock pressure which does not result in direct explosion, the low−velocity reaction wave propagates inside the sample for a certain amount of time, and the phenomenon is transferred to the C−J detonation state after that.

Keywords : Detonation, Tri−n−butyl phosphate, Fuming nitric acid, Velocity measurement

1. Introduction

The PUREX (Plutonium and Uranium Recovery by EXtraction) method applied to a spent nuclear fuel reprocessing process generally employs tri−n−butyl phosphate (TBP) and nitric acid. Presently, PUREX using TBP and nitric acid is performed safely under normal conditions. However, in the past, four explosion accidents originated from the use of this mixture[1,2]. These accidents indicate that the mixture of TBP and nitric acid is a high−potential explosion hazard.

Hence, study on the potential of explosion hazards of the TBP/nitric acid mixture has become an important subject. Our previous research studied the detonability of TBP with a high concentration of nitric acid. The results demonstrated that a mixture of TBP and fuming nitric acid (FNA) is detonated upon application of a shock ignition stimulus[3]. Then, the TBP/FNA mixture was shown to have a critical thickness of detonation propagation and explosion strength similar to that of liquid explosives[4,5]. When the card gap tests were performed, the results showed that three different kinds of deformation results appeared in the witness plate corresponding to differences in incident shock pressure[6−8].

In this paper, therefore, the results measuring the detonation velocities of the TBP and FNA mixture by optical and electrical methods are reported, in order to consider the difference in the reaction by incident shock pressure.

2. Experiments

2.1 Velocity measurement by the optical method

TBP/FNA=22/78 wt% of chemical equivalence ratio mixture was used for the sample. Initial temperature and density of the sample were 293.15 K and 1322 kg・m^{-3}, respectively. The assembly is shown in Figure 1. The sample container is a transparent polyvinyl chloride (PVC) tube (inner diameter of 20 mm, thickness of 3 mm) or a glass tube (inner diameter of 20 mm, thickness of 2.4 mm), and length is 200 mm. An exploding bridge wire type electric detonator (Nippon Kayaku Co., Ltd.) was used for the ignition of a booster explosive, pentolite of 34 g (1600 kg・m^{-3} in density, Chugoku Kayaku Co., Ltd.). In the case of the PVC tube container, four kinds of PMMA gaps (thickness

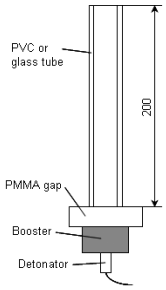

Figure 1 Assembly for optical method experiments.

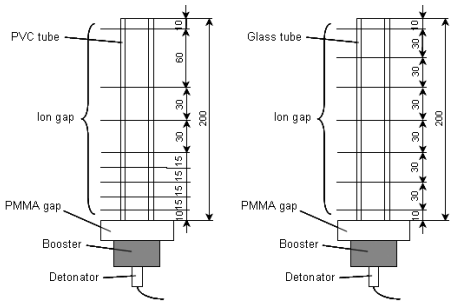

Figure 2 Assembly for electrical method experiments.

of 15, 20, 23, 25 mm) were installed between the booster explosive and the sample. In the case of the glass tube container, the experiments were conducted by installing five kinds of PMMA gaps (thicknesses of 10, 15, 20, 23, and 25 mm) between the donor explosive and the sample container. In case of the gap length of 25 mm, no detonation was considered to have occurred, from the card gap test result[6,7].

A streak camera (CORDIN, MODEL−116) was used for photography. Since the spontaneous light of the sample was weak, a krypton flash was used as a backlight source. A pulse generator (Berkeley Nucleonics Corp., BNC−555) was used for the synchronization of an explosion signal and the trigger signal for measurement.

2.2 Velocity measurement by the electrical method

The outline of the experimental assembly is illustrated in Figure 2. The kind of the sample and the container used here are the same as those of the previous section. Twisted polyester enameled copper wire with a diameter of 0.2 mm was used as the ion gap to detect the location of the reaction wave front. The ion gap was protected by winding fluoride tape around the portion in contact with the sample. Pulse generating equipment (Yatoro Denshi, Model−223 HV) was used, and the signals were recorded by a digitizing oscilloscope (Tektronix, TDS 3014 B).

The experiments were conducted using the PMMA gap material. For the PVC tube container, gap thicknesses of 15, 20 mm were used, and for the glass tube container, gap thicknesses of 5, 15 mm were used.

Table 1 Experimental results obtained by the optical method.

Container material	PMMA Gap thickness(mm)	Reaction wave velocity (km·s^{-1})	
		Low order	High order
PVC	15	1.83	6.53
PVC	20	1.83	6.53
PVC	23	1.83	6.53
PVC	25	1.83	−
Glass	10	−	6.44
Glass	15	−	4.81
Glass	20	−	4.66
Glass	23	−	4.80
Glass	25	−	4.81

3. Results and discussion

3.1 Reaction wave velocity obtained by the optical method

Figure 3 shows, as an example of streak photography, the result which was obtained for a gap length of 15 mm and a PVC tube container. The slopes of the straight lines (white) in the figure represent the propagation velocities of the wave fronts. Two velocities were observed under this experimental condition. All experimental results are summarized in Table 1. The velocity of approximately 6.5 km·s^{-1} is the C−J detonation velocity of the TBP/FNA mixture, as obtained from past research and calculation result[3,4].

Because in this experiment backlight was observed to be interrupted by the phenomenon, the measured low velocity has a high possibility of being the destruction speed of the sample container. This can also be guessed from it being nearly the same speed as the result of a gap length of 25 mm, a condition under which the sample will not detonate.

Moreover, as listed in Table 1, the phenomenon in which speed changed on the way was observed only for the PVC tube container, and it was not recordable for the glass tube container. For the same gap length, a similar phenomenon

Figure 3 An example of a streak photograph obtained by the optical method (PVC tube, 15 mm gap).

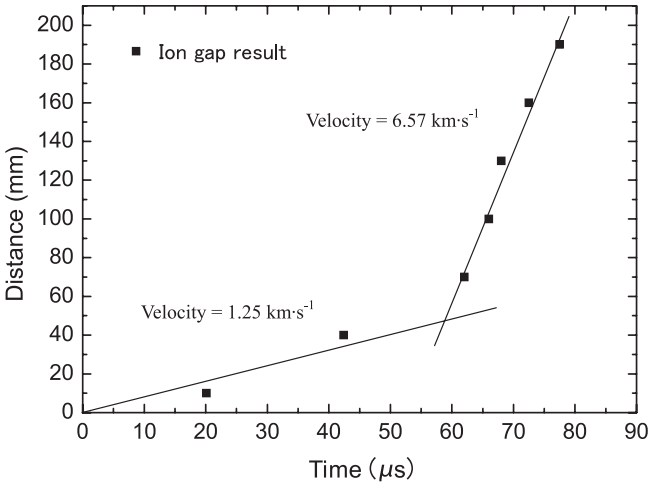

Figure 4 Relation of time and distance obtained by the electrical method (glass tube, 15 mm gap).

Table 2 Experimental results obtained by the electrical method.

Container material	PMMA Gap thickness (mm)	Reaction wave velocity (km·s^{-1})	
		Low order	High order
PVC	15	0.78	6.58
PVC	20	0.49	6.58
Glass	5	–	6.59
Glass	15	1.25	6.57

should be observed even if the physical properties of the sample container are different. This may be a result peculiar to the optical measurement method which uses a backlight. Thus, in the present study, measurements by the electrical method were also performed for the same sample container.

3.2 Reaction wave velocity obtained by the electrical method

Figure 4 shows the result of plotting the short circuit time of the ion gap and the relation to the distance; for the conditions of a glass tube container and a gap length of 15 mm. The two straight lines in the figure represent the result of linear fit for averaged or raw experimental data, and their slopes show the reaction wave velocity. Table 2 summarizes all the measurement results obtained by the electrical method. From the results of our previous work[7], the shock pressures in the PMMA gap material were estimated as 11.3 GPa (5 mm), 5.5 GPa (15 mm), and 4.1 GPa (20 mm).

Unlike the result of the optical method, also for the glass tube container, the two velocities were clearly observed; that is, the low velocity (1.25 km·s^{-1}) state up to 60 ms after initiation, and the C–J detonation velocity (6.57 km·s^{-1}). This shows that upon occurrence of a weak shock that does not directly result in explosion, the shock wave that propagates inside the sample may transfer to the C–J detonation state after a certain time delay. This is very important knowledge for the issue of safety. Also, this low-velocity propagation phenomenon of the reaction wave front might be low-velocity detonation rather than deflagration.

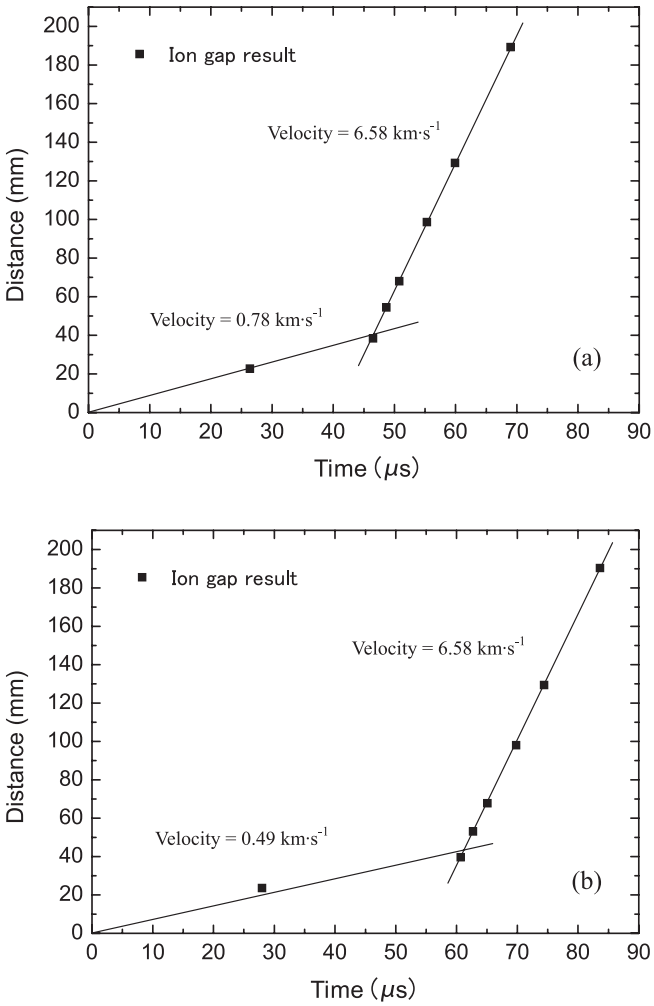

Figure 5 Relation of time and distance obtained by the electrical method (a) : PVC tube, 15 mm gap, (b) : PVC tube, 20 mm gap.

Meanwhile, in the case of the PVC tube container (Figs 5 (a) and 5 (b)) velocities less than 1 km·s^{-1} were observed. In these cases, the advance of the deflagration wave front seems to have been observed. Comparison of Figs. 4 and 5 (a) shows that the transient time from the low-velocity region to the C–J state is influenced by the sample container material. Namely, for a given gap thickness (same incident pressure), the time of transfer to the C–J detonation state with the PVC tube is much shorter than that with the glass tube. Comparison of Figs. 4 and 5 (b) shows that transition to the C–J detonation may take place even when the velocity of the low-velocity reaction wave front differs by a factor of 2.6, depending on the material of the container to be used. This constitutes other important knowledge for the issue of safety.

4. Conclusion

In order to consider the difference in the reaction phenomena of TBP/FNA mixture by incident shock pressure, velocity measurements of the reaction wave front have been conducted by optical and electrical methods.

The results show that the TBP/FNA mixture explodes by different mechanisms according to the strength of the incident shock pressure. That is, for a strong incident

shock pressure, the reaction propagates in the state of C−J detonation from the beginning, and for a weak incident shock pressure that does not result in direct explosion, a low−velocity reaction wave front propagates inside the sample for a certain amount of time, and the phenomenon subsequently transforms to the C−J detonation state.

Acknowledgments

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衝撃加圧によるリン酸トリ-n-ブチル/発煙硝酸混合物の反応伝播

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入射衝撃圧力による反応状況の違いを調べる目的で，リン酸トリ−n−ブチル（TBP）／発煙硝酸（FNA）混合物の反応伝播速度を光学的，電気的手法で測定した結果を報告する。入射衝撃圧力の強さにより，TBP／FNA 混合物が異なるメカニズムで爆発することわかった。すなわち，強い入射衝撃圧力では，反応は始めから C−J 爆轟状態で伝播し，直接起爆が起きない弱い入射衝撃圧力では，低速の反応波がある時間，試料中を伝播し，その後，現象は C− J 爆轟状態へ転移する。

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