Analysis of underwater explosion gas products of aluminum/ potassium chlorate mixtures

Tadahiro AOCHI*, Takehiro MATSUNAGA*, Yoshio NAKAYAMA*, Mitsuaki IIDA*, Atsumi MIYAKE**, and Terushige OGAWA**

A balloon test was carried out using the aluminum/potassium chlorate mixtures, and the underwater gas products were analyzed, in order to understand the underwater explosion phenomena of aluminum and oxidizer compositions of fireworks and to reveal the effects of morphology and contents of aluminum upon the bubble energy released by underwater explosion. As a result, a remarkable amount of hydrogen was detected and it was found that part of the aluminum powders in the sample mixtures reacted with the surrounding water. However, no correlation was found between the amount of hydrogen and the bubble energies obtained by the underwater explosion test. Thus, the reaction of aluminum with water should give a small contribution to the bubble energy

1. Introduction

Aluminum and oxidizer compositions have been widely used for fireworks, however, these compositions have been involved in a large number of serious accidents in the firework industries. In order to prevent and reduce the number of accidents and to minimize the damage due to undesired explosions in firework factories, the quantitative information about the explosion properties of pyrotechnic compositions containing aluminum powder and the safety evaluation on it are required.

In previous papers, in order to evaluate the explosion strength of firework compositions which contain potassium chlorate mixed with different kinds of aluminum, an underwater explosion test was carried out[1)-3)]. It was found that the shock and bubble energies produced by these mixtures were strongly influenced by the morphology of the aluminum powder and the energy releases of the Al/$KClO_3$ mixtures depended on the bubble energy compared to the shock energy. The maximum bubble energy value evaluated was at amount of 180% of that of TNT for a 50wt.% atomized aluminum content.

It is known that the explosives containing aluminum produce a large amount of bubble energies in the underwater explosion test, although the amount of the shock energy is not so large. Stmse showed the possibility of overestimating the bubble energy due to the reaction of aluminum in the sample and surrounding water in which releases hydrogen[4)]. However, the reaction of aluminum with the surrounding water has not been experimentally verified and the influence of the hydrogen on the bubble energy has not been quantitatively estimated either. In this paper, in order to understand the underwater explosion phenomenon of aluminum and oxidizer compositions and to reveal the effects of morphology and contents of aluminum upon the bubble energy released by underwater explosion, the gas products of the Al/$KClO_3$ mixtures were collected by a balloon and analyzed with the gas chromatography.

*Received on December 11, 1999
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305-8565 JAPAN
TEL 0298-61-4785
FAX 0298-61-4783
**Department of Safety Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 JAPAN
TEL 045-339-3992
FAX 045-339-4011

2. Experimental

2. 1 Materials

Table 1 shows the materials used in this study. The materials included flake aluminum [Al(f)] coated with stearic acid, atomized aluminum [Al(a)] spheroidal particles, and potassium chlorate [$KClO_3$] pyrotechnic grade. Their average particle diameters (and specific surface area) were 30 μm (3.55m^2/g), 20 μm (0.71m^2/g), and 70 μm (0.27m^2/g), respectively. All purities were greater than 99%. Both aluminums were manufactured by Nakatsuka Kinzoku Hakufun Kogyo Co., Ltd. Potassium chlorate was manufactured by Eka Nobel Elektrokemi. All materials had been stored in dry air at room temperature. The sample was mixed in a rotating mixing machine to form the binary mixtures. The theoretical zero oxygen balance for the Al/$KClO_3$ mixtures is a 30wt.% aluminum content.

2. 2 Balloon test

The balloon test was developed as a method to trap not only the solid reaction products but also the gaseous and dissolved products from the underwater explosion[6)-8)]. The experimental arrangement of the balloon test is shown in Fig. 1. A flexible natural rubber balloon made originally for weather observations with the radius of 0.31m and 0.2kg weight (manufactured by The Weather Balloon mfg. (Kikyu Seisakusho) Co., Ltd., Tokyo, Japan) was filled with about 0.125m^3 water and was suspended by wire in water-filled cylindrical open-topped firing tank with a diameter of 1.06m and a depth of 1.22m. A 1.5g test sample was loaded in a polyethylene vessel (diameter of 8.8mm and depth of 46.8mm) and a No.6 detonator was inserted into the vessel as shown in Fig. 2. The charge was suspended within the water in the balloon and placed as close as possible to the center of the balloon. The balloon was purged of any air bubbles and plugged with a silicone rubber stopper. The balloons were washed prior to the tests to remove the talc which were coated on the internal surface on the balloon during manufacturing.

When the amount of sample was less than 1.5 g, the balloon oscillated with the explosion bubble, but did not rupture. All gaseous

Table 1 Samples used in this study

Oxidizer	Al	Al content [wt.%]
$KClO_3$	Al(f)*	10,30,50
	Al(a)*	10,30,50

Al(f)* : flake aluminum
Al(a)* : atomized aluminum

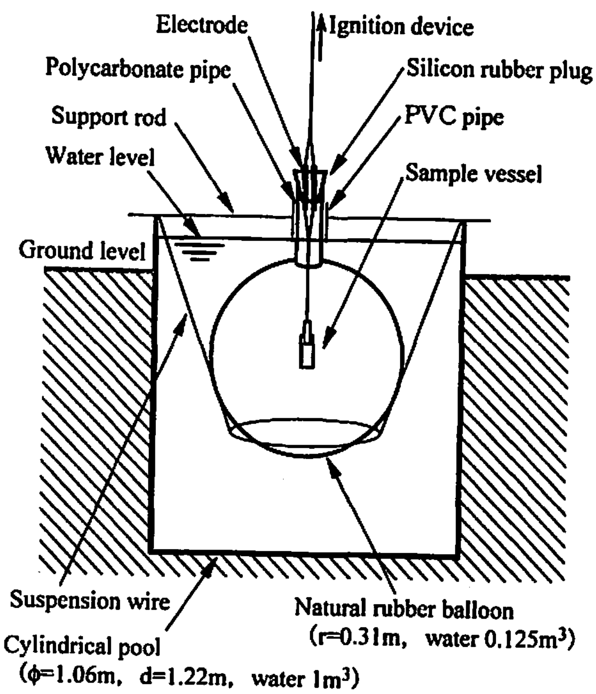

Fig. 1 Samples used in this study

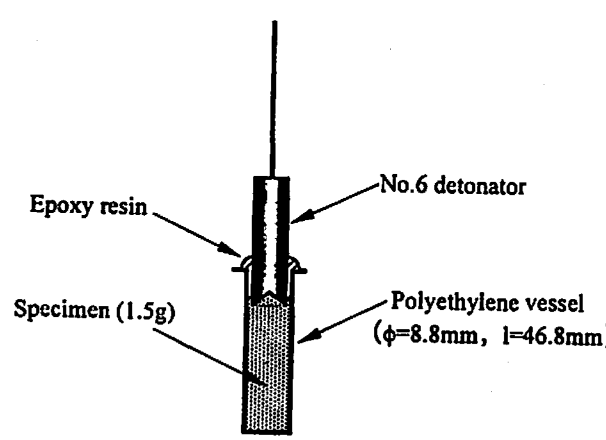

Fig. 2 Conditions for gas chromatography analysis

products of the explosion were trapped inside the balloon. After the total gas volume was measured using a 1000 ml graduated cylinder, a part of gaseous products were captured in a gas-sampling bottle for analysis. Product gases were analyzed by GC/TCD (Shimadzu Co., Ltd., GC6AM). Table 2 shows the conditions used to perform the analysis.

The ultimate purpose of the balloon test was to obtain data on the explosion of aluminum/oxidizer mixtures. In order to establish an experimental baseline, the initial test was performed using CHNO explosives. A No.6 detonator was chosen as the standard charge for calibration because it is easy to deal with and the detonation of the explosives inside the detonator is not easily influenced by the external conditions. Moreover, most of the explosion products do not chemically react with the surrounding water. The No.6 detonator used in this experiment consists of 0.2g of DDNP and 0.4g of tetryl.

2. 3 Underwater explosion test

The experimental arrangement was almost the same as that for the underwater explosion test given in previous papers[1)-3)]. The test was carried out in a round pool with a diameter of 8m and a depth of 5m. The charges were placed at a depth of 2.0m, and 0.5m from a tourmaline piezoelectric gauge. The pressure profiles of the shock waves and the bubble pulses were measured with the gauge and the pressure-time histories from the gauge were recorded with A/D converter connected to a personal computer.

A 1.5g test sample was loaded in a polyethylene vessel the same as that of the balloon test and was ignited by the No.6 detonator. The shock energy (E_s) and the bubble energy (E_b) were determined in the same way as shown in a previous paper[3)].

3. Results and Discussion

3. 1 Underwater explosion gas products of the Al/$KClO_3$ mixtures

The total gas volume and the ratio of each component obtained from the balloon tests of a detonator and of the sample charges (1.5g of Al/$KClO_3$ mixtures detonated by a detonator) are shown in Table 3. Five gas products were selected for our experiment, such as hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon monoxide (CO), and carbon dioxide (CO_2).

In order to estimate the amount of leakage of the gas products and the contamination to the sampling gas, material balances between the calculated values from the compositions of explosives in the detonator and the elements

Table 2 Conditions for gas chromatography analysis

H_2 Analysis	Column	Molecular Sieve 5A
	Carrier Gas	N2, 40ml/min
	Sample mass	0.5ml
	Temperature	40℃
CO_2 Analysis	Column	Porapak N
	Carrier Gas	He, 40ml/min
	Sample mass	1ml
	Temperature	50℃
All gases except H_2 and CO_2	Column	Molecular Sieve 5A
	Carrier Gas	He, 40ml/min
	Sample mass	1ml
	Temperature	50℃

contained in the sampling gas were considered as shown in Table 4. Concerning the results of the detonator, although the amount of the carbon, hydrogen and oxygen elements in the sampling gas were less than those of the calculated values, the amount of nitrogen showed a good agreement with the calculated value. It is expected that CO_2 dissolved in the water, hydrogen was chemically converted into liquefied H_2O, and the carbon was chemically converted into solid carbon. Concerning the results of the Al/$KClO_3$ mixtures, the amount of N was 10~25% more than the experimental values obtained from the detonator. It was thought that there was some contamination, such as air in the sample vessel that gets into the sampling gas. The balance of nitrogen is found to be useful to verify the experimental success, because the sample composition and the Al/$KClO_3$ mixtures does not contain any nitrogen.

Table 3 Major underwater explosion gas products in the balloon test

Sample	Total gas volume [$\times 10^{-6}$ m^3]	Each gas products [vol.%]					
		H_2	O_2	N_2	CO	CO_2	CH_4
No.6 detonator	320 339	5.4 5.2	5.2 4.4	45.5 43.0	43.0 43.8	2.9 3.6	0.5 0.0
Al(f)/$KClO_3$=10/90	466	2.2	35.1	36.0	22.1	4.7	0.0
Al(f)/$KClO_3$=30/70	427 433	15.6 22.9	6.3 3.7	41.7 37.5	35.9 34.2	1.7 1.7	0.3 0.0
Al(f)/$KClO_3$=50/50	598 587	30.5 36.2	3.7 2.7	28.6 27.2	32.8 32.8	3.6 1.8	0.2 0.0
Al(a)/$KClO_3$=10/90	435	2.0	28.2	37.5	25.1	3.2	0.0
Al(a)/$KClO_3$=30/70	467 445	19.0 21.2	4.8 5.3	36.4 37.3	34.1 33.1	2.4 1.9	0.0 0.0
Al(a)/$KClO_3$=50/50	612	37.6	4.8	30.3	29.4	1.8	0.0

Table 4 Material balances of underwater explosion gas products

Sample	Amount of each element [vol.%]			
	C	H	N	O
Calculated from a detonator	1.55×10^{-2}	8.87×10^{-3}	1.08×10^{-2}	1.59×10^{-2}
No.6 detonator	6.03×10^{-3} 6.53×10^{-3}	1.64×10^{-3} 1.43×10^{-3}	1.18×10^{-2} 1.18×10^{-2}	7.70×10^{-3} 8.22×10^{-3}
Al(f)/$KClO_3$=10/90	5.08×10^{-3}	8.18×10^{-4}	1.36×10^{-2}	1.92×10^{-2}
Al(f)/$KClO_3$=30/70	6.58×10^{-3} 6.33×10^{-3}	5.63×10^{-3} 8.04×10^{-3}	1.45×10^{-2} 1.32×10^{-2}	9.01×10^{-3} 7.94×10^{-3}
Al(f)/$KClO_3$=50/50	8.89×10^{-3} 8.23×10^{-3}	1.50×10^{-2} 1.73×10^{-2}	1.39×10^{-2} 1.30×10^{-2}	1.15×10^{-2} 9.93×10^{-3}
Al(a)/$KClO_3$=10/90	4.99×10^{-3}	7.00×10^{-4}	1.32×10^{-2}	1.55×10^{-2}
Al(a)/$KClO_3$=30/70	6.93×10^{-3} 6.32×10^{-3}	7.20×10^{-3} 7.67×10^{-3}	1.38×10^{-2} 1.35×10^{-2}	9.20×10^{-3} 8.56×10^{-3}
Al(a)/$KClO_3$=50/50	7.74×10^{-3}	1.87×10^{-2}	1.51×10^{-2}	1.05×10^{-2}

Fig. 3 shows the influence of the aluminum content and the morphology of the aluminum particles on the total volume of gas products from the explosion of 1.5g Al/$KClO_3$ mixtures detonated by the detonator. The plots in this figure show the amount of gas products produced from both the sample composition and the detonator used in each experiment. It was found that there was little difference in the total gas volume between Al(f)/$KClO_3$ and Al(a)/$KClO_3$ with the same aluminum content. The total gas volume at 10 and 30wt.% aluminum content, i.e., positive oxygen balance condition, was almost the same. On the other hand, the total gas volume at 50wt.% aluminum content, i.e., negative oxygen balance condition, was 30% more than those of 10 and 30wt.% aluminum content. Thus, the total gas volume was significantly influenced by the aluminum content and oxygen balances of the samples.

Fig. 4 and 5 show the influence of the aluminum content and the morphology of aluminum particles on the amount of each gas product. Fig.4 shows the amount of N_2, CO, and CO_2. These three products were considered to be produced from the detonator used to ignite the sample. Kato et al. suggested that the aluminum reacted with N_2 as well as H_2O and CO_2 and the reactions contributed to bubble energy release when emulsion explosive containing aluminum powder were detonated underwater[8]. However, in our study, the amount of N_2 did not change as the aluminum content increased. As shown in Table 4, the amount of N elements from explosion is almost the same as that of the detonator. Thus, in the underwater explosion of Al/$KClO_3$ mixture, N_2 did not react with aluminum and the other gaseous products from the detonator. On the other hand, the amount of CO increased with an increase in the aluminum content. This is because the following reaction occurs as the sample contains excess aluminum[9].

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO \quad (1)$$

However, the amount of aluminum reacted with CO_2 based on equation (1) is evaluated to be less than 0.2%. Thus, in the balloon test of the Al/$KClO_3$ mixtures, the reaction of aluminum with N_2 and CO_2 from the detonator may be negligible.

Fig. 5 shows that the amount of O_2 in the gas products was relatively high, at 10wt.% aluminum content, i.e., positive oxygen balance condition for both Al(f)/$KClO_3$ and Al(a)/$KClO_3$. It was considered that excess $KClO_3$ in the sample thermally decomposed to produce O_2 and the reaction was given as follows.

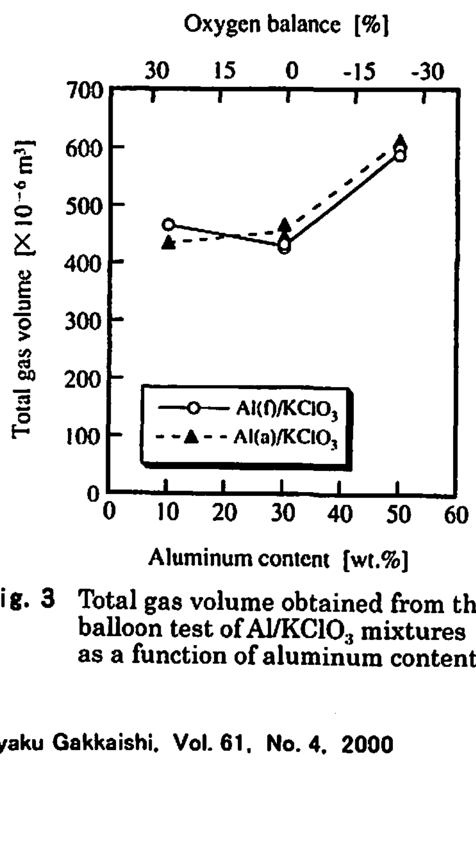

Fig. 3 Total gas volume obtained from the balloon test of Al/$KClO_3$ mixtures as a function of aluminum content

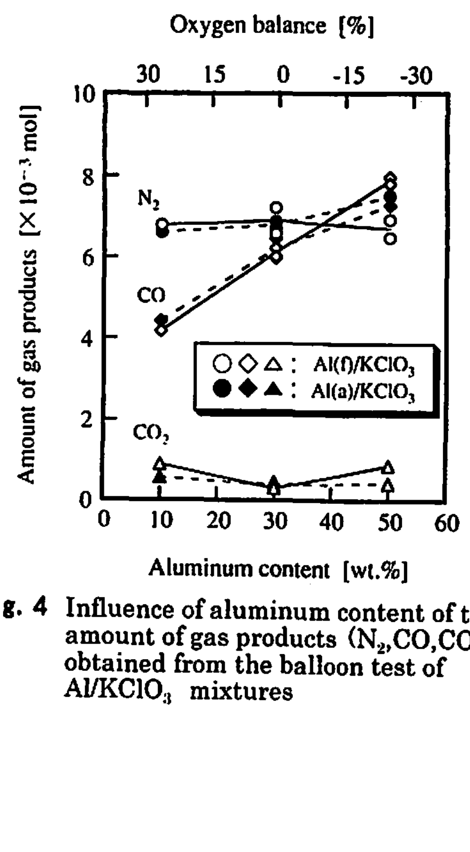

Fig. 4 Influence of aluminum content of the amount of gas products (N_2,CO,CO_2) obtained from the balloon test of Al/$KClO_3$ mixtures

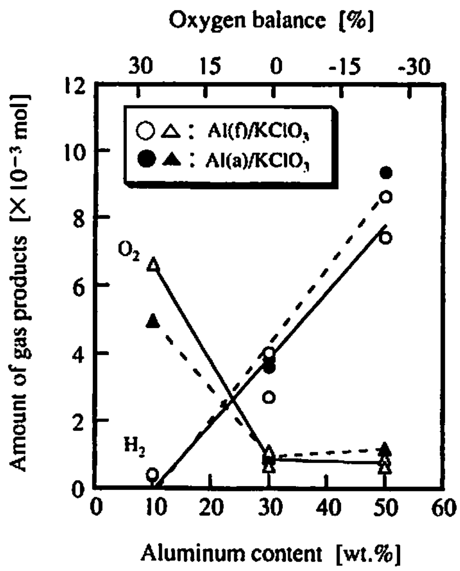

Fig. 5 Influence of aluminum content on the amount of gas products (H_2,O_2) obtaind from the balloon test of Al/$KClO_3$ mixtures

$$2KClO_3 \rightarrow 2KCl + 3O_2 \qquad (2)$$

Fig. 5 shows that H_2 was produced at the 30 and 50 wt.% aluminum contents, i.e., negative oxygen balance conditions, and its amount increased as the aluminum content increased. It was clear that H_2 was produced from the reaction of the aluminum in the sample with the surrounding water because the sample compositions did not contain hydrogen. The reaction of aluminum with water is known and the reaction schemes are very complicated, and varied with the reaction temperature range[10)-15)]. Some reaction schemes have been suggested in previous studies. It is considered that the reactions of aluminum with water are basically the same reaction as the hydration of aluminum. Some possible reactions are as follows:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \qquad (3)$$

$$2Al + 4H_2O \rightarrow 2AlOOH + 3H_2 \qquad (4)$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \qquad (5)$$

It is expected that the main reaction follows equation (3). It is known that the hydration of aluminum occurs over 100℃, without an induction period. The results of our experiment clarified that part of aluminum powders in the sample reacted with the surrounding water during the underwater explosion test and the reaction produced a significant amount of hydrogen.

3.2 The influence of the hydrogen on the bubble energies of the Al/$KClO_3$ mixtures

In order to confirm the influence of the hydrogen from the reaction of aluminum with the surrounding water on the bubble energies of the Al/$KClO_3$ mixtures, the underwater explosion test of a 1.5g test sample, which was loaded in a polyethylene vessel that was the same as that of the balloon test, was carried out. Fig. 6 shows the influence of the morphology of the aluminum particles on the shock energies of the explosion of Al/$KClO_3$ mixtures as a function of aluminum content. The shock energies of 1.5g of Al(f)/$KClO_3$ showed a maximum value at 20wt.% aluminum content, i.e., positive oxygen balance condition. As the aluminum content increased, the shock energies significantly decreased at more than about 30wt.% aluminum content, i.e., negative oxygen balance conditions. The trend of shock energy change with aluminum content of 25g of Al(f)/$KClO_3$ was almost the same as that of 1.5g of Al(f)/$KClO_3$. The difference of shock energies between 1.5g and 25g of the mixture may be due to its low reactivity. On the other hand, Al(a) mixed with $KClO_3$ showed a maximum value at 30wt.% aluminum content.

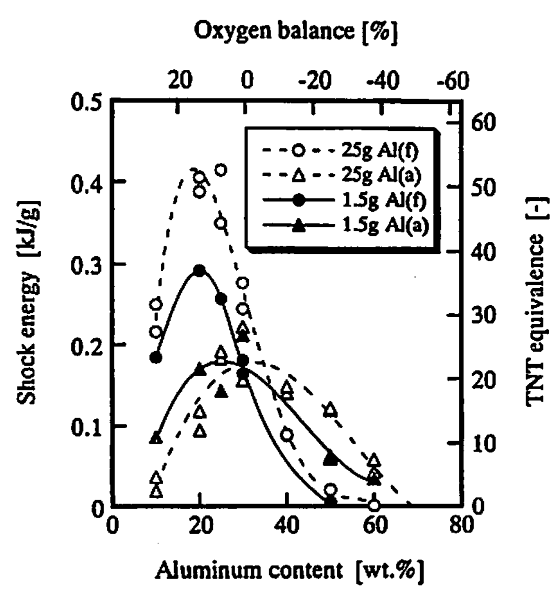

Fig. 6 Shock energies of Al/$KClO_3$ mixtures as a function of aluminum content

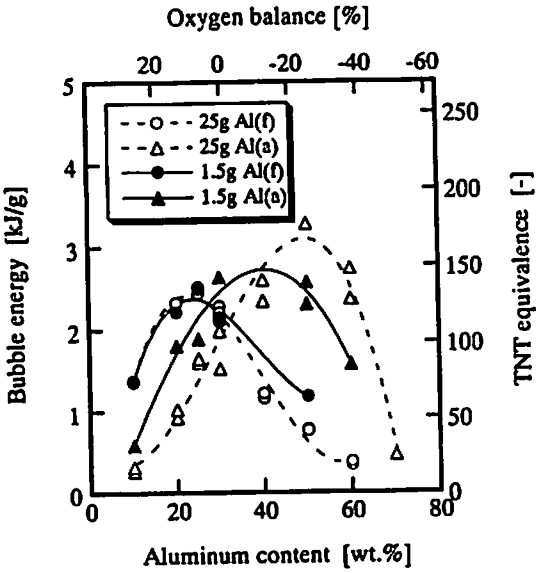

Fig. 7 Bubble energies of $Al/KClO_3$ mistures as a function of aluminum content

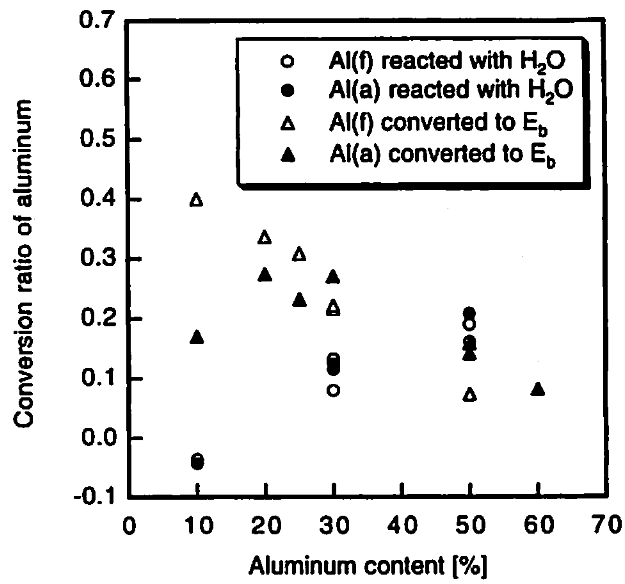

Fig. 8 Conversion ratio of aluminum to the reaction with water and to the bubble energy as a function of aluminum content of $Al/KClO_3$

There are two possible ways to cause a reaction between aluminum and water. First, the unreacted aluminum powder with contacts water on the surface of a bubble during the first bubble oscillation. Second, the unreacted aluminum powder contacts with water while the bubble is rising to the surface after the first bubble oscillation. If the first one is correct, there should be a correlation between the amount of hydrogen and the bubble energy. Fig. 7 shows the influence of the morphology of the aluminum particles on the bubble energies of the explosion of $Al/KClO_3$ mixtures as a function of aluminum content. The bubble energies of Al(f) mixed with $KClO_3$ showed a maximum value at 25wt.% aluminum content, i.e., positive oxygen balance conditions. On the other hand, Al(a) mixed with $KClO_3$ showed a maximum value at 30~50wt.% aluminum content, i.e., negative oxygen balance conditions. It is clear that there is no correlation between the amount of hydrogen determined by the balloon test and the bubble energies. Moreover, Fig. 8 shows the calculated conversion ratio of aluminum in the sample to the reaction with water and to the bubble energy. The conversion ratio of aluminum with water is based on the amount of hydrogen and equation (3). The conversion ratio of aluminum to the bubble energy is based on $E_b/\Delta H$. ΔH is based on the following equation.

$$2Al + KClO_3 \rightarrow Al_2O_3 + KCl \qquad (6)$$

The heat of reaction, ΔH has a maximum value, when the oxygen balance is nearly zero (the aluminum content is about 30 %). However, as the aluminum content increases, the conversion ratio of aluminum in the reaction with water increases linearly, and oppositely that to the bubble energy decreases. Thus, there is no correlation between these conversion ratios and the heat of reaction, ΔH. And the tendency shown in Fig.8 showed that the aluminum not converted to the bubble energy should reacted with water, although the reaction had little influence on the bubble energy. Moreover, it is suggested that there is an other reason for the large bubble energy observed during the underwater explosion test of aluminum/oxidizer mixtures[16].

In a previous paper[2], we reported that a strong light emission was observed during the first bubble oscillation of the gas bubble from the underwater explosion of the $Al/KClO_3$ mixtures using a high-speed video record. Moreover, we reported that the band spectra of AlO were observed inside the light of the first bubble oscillation using a spectroscopic method[18]. AlO is one of the intermediate gaseous reaction products of aluminum/oxidizer mixtures based on an equilibrium calculation[19]. These facts show that the combustion of the aluminum particles does not finish instantaneously, but continues to burn from the surface into the inside of the particles while the gas bubble was expanding and contracting. The total amount of intermediate gas product from the combustion of aluminum becomes large. That is, it is considered that the large bubble energies of the aluminum/oxidizer mixtures are caused not by the reaction of aluminum with the surrounding water, but by the afterburning of aluminum powders inside the gas bubble during its expansion. We need to quantitatively estimate the influence of the afterburning phenomena of aluminum on the bubble energies.

4. Conclusion

From the experimental investigation of underwater explosion gas products of aluminum/potassium chlorate mixtures using the balloon test, the following conclusions can be drawn:

(1) A part of aluminum powder in the aluminum /oxidizer mixtures reacted with the surrounding water during the underwater explosion test and the reaction produced a remarkable amount of hydrogen.

(2) There is no correlation between the amount of hydrogen detected by the balloon test and the bubble energies and it is understood that the reaction of aluminum with water provided only a small contribution to the bubble energy release.

References

1) T.Aochi, A.Miyake, T.Ogawa, T.Matsunaga, Y.Nakayama and M.Iida, Journal of the Japan Explosives Society, 58, 202-210 (1997)

2) T.Aochi, A.Miyake, T.Ogawa, T.Matsunaga, Y.Nakayama and M.Iida, Proc. 22nd Pyrotechnics Seminar, 23-34, Fort Collins (1996)

3) T.Aochi, A.Miyake, T.Ogawa, T.Matsunaga, Pyrotechnics Seminar, 26-36, Tsukuba (1997)

4) E.Stmse and S.W.Eriksen, Propellants, Explosives, Pyrotechnics, 15, 52-53 (1990)

5) D.Carlson, R.Doherty, V.Ringbloom, J.Deiter and G.Wilmot, Proc. 9th Int'l Symposium on Detonation, 626-632, Chicago (1989)

6) F.Volk, F.Schedlbauer, Proc. 19th Int'l Pyrotechnics Seminar, 631-637, Christchurch (1993)

7) F.Volk, F.Schedlbauer, Proc. 10th Int'l Symposium on Detonation, 601-607, Bostons (1993)

8) Y.Kato, K.Takahashi, A.Torii, K.Kurokawa and K.Hattori, Proc. 30th Int'l Annual Conference of ICT, 7_1-10, Kahlsruhe (1999)

9) F.Volk and F.Schedlbauer, Propellants, Explosives, Pyrotechnics, 18, 332-336 (1990)

10) B.Lurie, L.Skopintseva, V.Lushkin, A.Chernyshov, Proc. 19th Int'l Pyrotechnics Seminar, 410-427, Christchurch (1993)

11) W.J.Bernard and J.J.Randall, Jr., J. Electrochemical Society, 483-487 (1960)

12) W.Vedder and D.A.Vermilyea, Trans. Faraday Society London, 65, 561-584 (1969)

13) A.S.Tompa and D.M.French, J. Hazardous Materialsrans, 2, 197-216 (1977/78)

14) R.S.Alwitt, J. Electrochemical Society, 1322-1328 (1974)

15) M.Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", 168-175 (1966) Pergamon press

16) T.Keicher, A.Happ and A.Kretshmer, Propellants, Explosives, Pyrotechnics, 24, 140-143 (1999)

17) Y.Nakayama, T.Matsumura, T.Matsunaga, M.Iida and M.Yoshida, Proc. 23rd Int'l Pyrotechnics Seminar, 608-615, Tsukuba (1997)

18) L.Brewer and A.W.Searcy, J. American Chemical Society, 73, 5308-5314 (1951)

19) M.L. Hobbs, K. Tanaka, M. Iida, T. Matsunaga, Proc. 3rd Beijing Int'l. Symp. On Pyrotechnics and Explosives, Beijing, China, 16 (1995)

アルミニウム/塩素酸カリウム混合物の水中爆発生成ガスの解析

青地忠浩*，松永猛裕*，中山良男*，飯田光明*，三宅淳巳**，小川輝繁**

アルミニウム粉末の形状およびその含有量がアルミニウム／酸化剤系煙火組成物の水中爆発におけるバブルエネルギーに与える影響を調べるために，水中爆発生成ガスを採取できるバルーンテストを行った。その結果，水中爆発生成ガスに大量の水素が計測された。これは，爆発後に試料中のアルミニウム粉末が爆源周囲の水と反応したためと考えられる。また，水素の生成量と水中爆発試験より得られたバブルエネルギー値との関係を調べた結果，両者の間にはあまり関係のないことが分かった。したがって，アルミニウム／酸化剤系煙火組成物の水中爆発においては，アルミニウムと水との反応による水素の発生は，バブルエネルギーにほとんど寄与していないことが示唆された。

(*物質工学工業技術研究所　極限反応部　〒305-8565 茨城県つくば市東1－1
**横浜国立大学　工学部　物質工学科　〒240-8501 横浜市保土ヶ谷区常盤台156)