Research paper

Effect of deterioration products in moisture on the thermal behavior of ammonium perchlorate/magnesium mixture

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Abstract
Specific mixtures of ammonium perchlorate (AP) and magnesium are used in fireworks and to demonstrate the strobe effect. The composition easily undergoes deterioration in the presence of moisture, but the effects of this deterioration are complex and not well-understood. This study aims to determine the effects of moisture-induced deterioration products on an AP/Mg mixture. The mixture was subjected to an accelerated aging test with moisture and by mixing the AP with deterioration products. Analysis of the thermal behavior of the samples revealed that the aging test decreased the heat generation and increased the onset temperature of the exothermic peaks. The addition of the deterioration product, magnesium hydroxide, had the same effect on AP. The effects of the material of vessels are slight. The onset temperature of the exothermic peaks for the AP/Mg mixture was slightly changed in the samples stored for durations ranging from 24-144 h, unlike the heat generation. Analysis of the Mg surface in the aged samples indicates that the products coated the Mg powders after the initial stage of deterioration. The thermal stability of AP is observed to be affected by the materials on the Mg surface, and hence, the initial stage of deterioration is effective for thermal stability.

Keywords: ammonium perchlorate, magnesium, fireworks, aging, moisture absorption

1. Introduction
Ammonium perchlorate (AP) is a common oxidizer that is a component of explosive mixtures such as fireworks, propellants, and other pyrotechnics. Occasionally, the oxidizer is mixed with Mg, which provides high brightness[1] and reduces the amount of generated toxic gases thereby lessening the environmental impact[2]. In addition, the AP/Mg mixture exhibits unique combustion properties called the strobe effect[1),3),4]. However, this mixture deteriorates easily in the presence of water[1]. There have been some investigations into the deterioration of AP/Mg because of the related issues[1),5]. It was found that the main deterioration product associated with moisture is magnesium hydroxide and the byproduct is magnesium perchlorate[6].

The generation of these deterioration products may affect the performance parameters of the compositions, such as combustion rate, flame color, and sensitivity. Understanding the changes in performance is important because it affects the quality and sometimes results in accidents due to changes in thermal behavior following unexpected or abnormal combustion. Therefore, this paper aims to determine the effects of moisture-induced deterioration on the thermal behavior of AP/Mg.

Several studies used thermal analysis to investigate the effects of aging on the composition of explosive devices[7)-9]. These studies reported the effects of deterioration products, with heat release and absorption accompanying the decomposition and/or reaction. The relationship between the thermal behavior and deterioration products was useful to determine important materials that are affected. Therefore, thermal analysis is considered an appropriate technique to explore the effects of aging duration and deterioration products.

In this study, deliberately aged compositions were measured by differential scanning calorimetry (DSC) in order to identify the effects of deterioration on thermal behavior. The samples were stored in humid conditions and obtained from an incubator after 0, 24, and 144 h. In addition, the effects of the materials used to make the vessels employed for DSC (glass and stainless steel) were verified and compared. The deterioration products were added to pure AP, and the effect of each deterioration product was compared with samples that were stored in humid air.

2. Experimental

2.1 Sample preparation

AP (Wako Special Grade: Wako Pure Chemical Industries, Ltd.), Mg (Mg-100: Kanto Metal Corporation), magnesium hydroxide ($Mg(OH)_2$, 99.9%: Wako Pure Chemical Industries, Ltd.), and magnesium perchlorate hexahydrate ($Mg(ClO_4)_2 \cdot 6H_2O$, 99%: Wako Pure Chemical Industries, Ltd.) were used without further purification. Deteriorated AP/Mg was obtained by performing an accelerated aging test in a sealed container where the samples were maintained under constant temperature and humidity. The temperature was controlled by an incubator and the internal humidity was maintained using saturated salts. The aged AP/Mg samples were obtained by performing an aging test at 40 °C and RH of about 75%. The storage conditions were determined by the results of previous investigations[6]. All the ratios of the materials in the samples are shown in Table 1. The ratio of AP/Mg was determined by referring to the ratio of fireworks compositions[10]. In order to observe the effect of the deterioration products, the ratios of the AP/$Mg(OH)_2$ and AP/$Mg(ClO_4)_2$ samples were determined based on the charge ratio between NH_4^+ and Mg^{2+}.

2.2 Measurements

The thermal behavior of the samples was measured by DSC. Some materials generate reactive substances when heated. Reactive substances can interact with the vessels during measurement and affect the DSC results. The phenomenon was reported for measurements involving stainless steel vessels (referred henceforth as stainless vessels), which is essential for sealed DSC experiments[11]. This could lead to problems during comparison between fresh and aged samples. Thus, in this study, two types of sealed DSC vessels, i.e., inert vessels and stainless vessels were used. The inert sealed vessels were made of glass (referred henceforth as glass vessels). The volume of the stainless vessels is 15 μL, while that of the glass vessels is about 100 μL. A Q200 (TA Instruments) was employed for experiments with stainless vessels, and a DSC 1 (Mettler Toledo International Inc.) instrument was employed for those with glass vessels. In each measurement, a vessel containing a sample was heated to 500 °C at 10 K min^{-1} and all experiments were carried out at least thrice.

Table 1 Lomposition of the DSC samples at sample preparation. (The ratios do not consider the effect of weight variation due to aging).

Name	Mass ratio [-] (Mole ratio [-])			
	AP	Mg	$Mg(OH)_2$	$Mg(ClO_4)_2 \cdot 6H_2O$
AP	1	–	–	–
AP/Mg	12 (1)	5 (2)	–	–
Aged AP/Mg (24) (24 [h] storage)	12 (1)	5 (2)	–	–
Aged AP/Mg (144) (144 [h] storage)	12 (1)	5 (2)	–	–
AP/$Mg(OH)_2$	1 (2)	–	1 (1)	–
AP/ $Mg(ClO_4)_2$	78(2)	–	–	100(1)

The surface state of the deteriorated AP/Mg was studied by SEM-EDX (JSM-7001F, JEOL Ltd.) under high vacuum conditions at an acceleration voltage of 15 kV. The ratio of the elements was calculated by the ZAF method and analyzed by TEAM™ EDS Analysis System. The measurement area was the Mg powder surface in AP /Mg mixtures. Each sample was measured after dry heating (100 °C, 0.5 h).

3. Results and discussion

3.1 Thermal analysis of aged AP/Mg samples

Results of the thermal analysis are shown in Figure 1 (glass vessels) and Figure 2 (stainless vessels). The obtained parameters (Table 2) represent the onset temperature of exothermic peaks (T_{onset}), peak temperature of exothermic peaks (T_p), and calorific value (Q).

It is observed that mixing AP and Mg results in a decrease of T_{onset} and increase of Q. Figure 1 also shows that the aging test altered the T_{onset}, T_p, and Q values of the fresh AP/Mg samples. After the aging test, the exothermic peaks appeared at a higher temperature compared to that before the test. Further, the heat generation decreased due to the deterioration of AP/Mg.

The effect of the material of the DSC vessel on the change in the thermal behavior was also verified. The DSC curves for the decomposition of AP were affected by the material of the vessel; in the stainless vessels, T_{onset} decreased and Q increased. The variation of Q indicates a change in the chemical reaction. This is believed to be due to the reaction between AP and stainless steel. Variation of T_{onset} was attributed to the catalytic effect of stainless steel against AP decomposition.

The exothermic peak of the AP/Mg samples was not significantly affected by the vessel's materials. It is believed that the reaction between AP and stainless steel was more difficult in AP/Mg than pure AP because it is relatively easy for Mg to react with AP. Additionally, stainless vessels provide better pressure resistance than glass vessels. Thus, the stainless vessels were used to

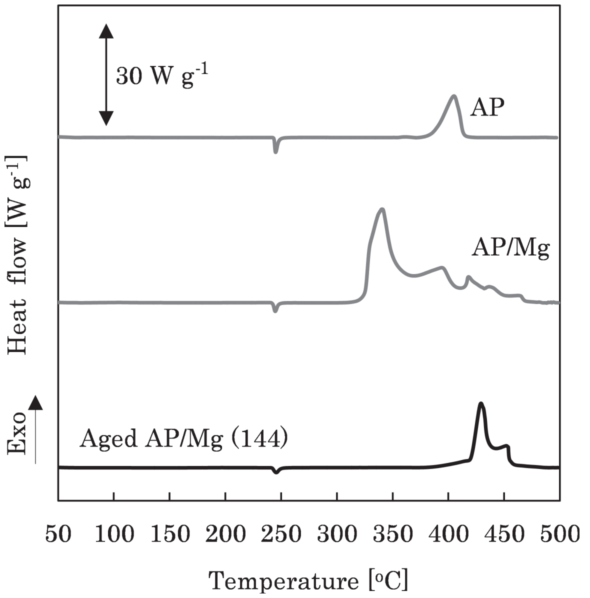

Figure 1 Thermal analysis results obtained using glass vessels.

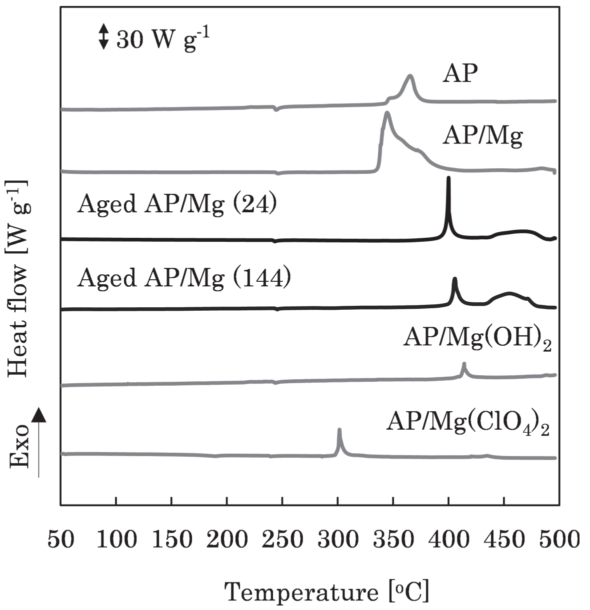

Figure 2 Thermal analysis results obtained using stainless vessels.

study the effects of deterioration from the perspective of the onset temperature of exothermic peaks and heat generation.

3.2 Effects of deterioration products on thermal behavior of AP/Mg

The increase in T_{onset} and the decrease in Q are believed to be a result of the deterioration products. For verification, the AP and deterioration product mixtures were measured by DSC. Each mixture, AP/$Mg(OH)_2$ and AP/$Mg(ClO_4)_2$, shows a lower Q than that of AP and AP/Mg (Table 2). However, AP/$Mg(ClO_4)_2$ exhibited a lower T_{onset} than AP and AP/Mg, suggesting that $Mg(ClO_4)_2$ is not primarily responsible for the change of T_{onset} in the aged AP/Mg samples. The exothermic peak of AP/$Mg(OH)_2$ appeared at the same temperature as the aged AP/Mg samples, indicating that $Mg(OH)_2$ was closely involved in the change in T_{onset}.

Table 2 Exothermic peaks observed in the thermal analysis.

	Name	T_{onset} [°C] (First exothermic peak)	T_p [°C]	Q [kJ g^{-1}]
Glass vessels	AP	381	394	1.4
	AP/Mg	330	345	9.1
	Aged AP/Mg (144)	420	430	2.4
Stainless vessels	AP	345	368	3.3
	AP/Mg	332	353	8.8
	Aged AP/Mg (24)	396	398	5.1
	Aged AP/Mg (144)	401	403	3.4
	AP/$Mg(OH)_2$	400	403	0.98
	AP/$Mg(ClO_4)_2$	301	304	1.0

Analysis of the effects of storage duration revealed that the heat generation decreased as the storage duration increased, but T_{onset} and T_p remained stable. A decrease in the heat generation implies that the deterioration products generate lower energy than AP/Mg. However, the stability of the T_{onset} indicates that the change of T_{onset} is complete after storage for 24 h.

The exothermic behavior of aged AP/Mg appeared at a higher temperature than AP. The increase of the thermal stability may be attributed to the coating of the deterioration products on Mg. The primary deterioration product, $Mg(OH)_2$, was generated on the Mg surface, covering it. This coating blocks the contact between AP and Mg, resulting in contact with $Mg(OH)_2$. Accordingly, the change in composition on the Mg surface was measured.

3.2 Observation of Mg surface in aged AP/Mg mixtures

The change in composition on the Mg surface in the aged AP/Mg mixture was measured by SEM-EDX. The morphology of the Mg surface (Figure 3) reveals that the deterioration products grew on the Mg surface and eventually covered it after storage for 72 h. The area on the Mg surface observed by a magnification of ×5000 was measured by EDX. EDX results (Figure 4, Table 3) revealed the corresponding ratios of elements on the Mg surface. First, the purchased Mg has a thin oxide coating. After aging, the ratio of O atoms and Cl atoms increased and that of Mg atoms decreased. This change in composition indicated the generation of the reported deterioration products[6], $Mg(OH)_2$ and $Mg(ClO_4)_2$, which were spread on the Mg surface.

When the Mg surface changes to $Mg(OH)_2$, the elemental ratios of oxygen and Mg should be 2:1. Figure 5 illustrates the ratio of O/Mg atoms as a function of the storage duration. The oxygen ratio was found to increase within 24 h and continued to increase slowly as the storage duration was extended. This behavior would explain the fact that the samples aged for 24 h showed significant change in the T_{onset}, while the samples aged for

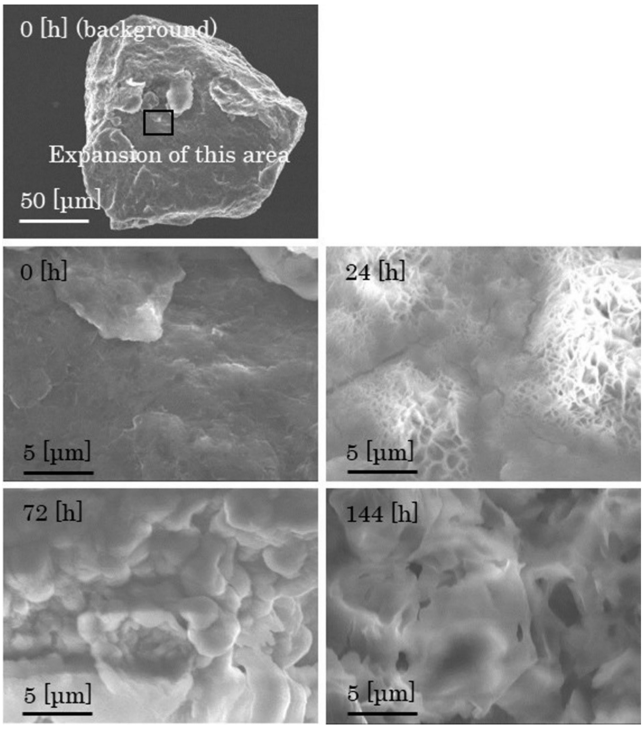

Figure 3 EDX images of the Mg surface in AP/Mg mixture during aging. The measured background for a sample stored for 0 h is shown for comparison.

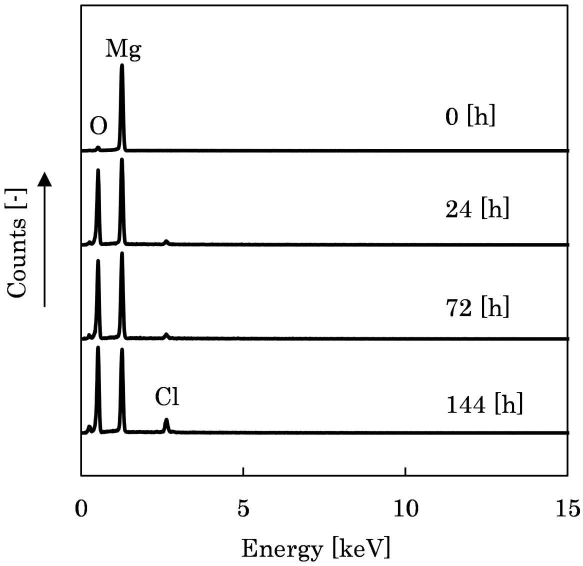

Figure 4 EDX results obtained on Mg surface in AP/Mg mixture during aging.

longer exhibited T_{onset} values that were only slightly higher.

4. Conclusions

In this study, the effect of aging on the thermal stability of AP/Mg was investigated. The results showed that exothermic peaks appeared at higher temperature than before the aging test and heat generation decreased owing to the aging test. The results show that moisture-induced deterioration results in changes in the thermal stability, causing unexpected performances of the pyrotechnics composition.

The vessels used for DSC measurements affected the thermal behavior of the AP samples. However, the effects were less obvious for the AP/Mg samples than the AP samples. This could be because AP reacted with the stainless vessels leading to changes in the thermal behavior; in the case of AP/Mg samples, however, AP reacted more easily with Mg than stainless steel.

The deterioration products of AP/Mg affected the AP decomposition temperature and heat generation. Analysis of the DSC results of aged AP/Mg and AP/deterioration product mixtures indicated that $Mg(OH)_2$ was mainly responsible for the changes in the onset temperature of the exothermic peaks during the aging.

The storage duration of the aging test decreased the heat generation of AP/Mg, but the temperature of exothermic peaks was similar after storage for 24 and 144 h. The heat generation was affected by the number of deterioration products; however, the decomposition of AP affected the reactant surface. It is considered that the products of deterioration were generated on the surface of the Mg powder, coating it. The SEM-EDX results were in good agreement with the hypothesis, and the surface deterioration was almost complete in the first 24 h of storage. The results indicate that the initial deterioration stage significantly affected the thermal stability of the AP

Table 3 EDX results of Mg surface in AP/Mg mixture.

	Elements	mol [%]	Error [%]
Before aging (Reagent)	O	18.7	10.32
	Mg	81.3	3.31
	Cl	–	–
Aged AP/Mg (24)	O	65.7	6.97
	Mg	32.3	4.95
	Cl	2.00	9.82
Aged AP/Mg (72)	O	68.6	8.88
	Mg	29.5	6.34
	Cl	1.9	18.48
Aged AP/Mg (144)	O	70.5	7.52
	Mg	25.9	5.29
	Cl	3.6	8.49

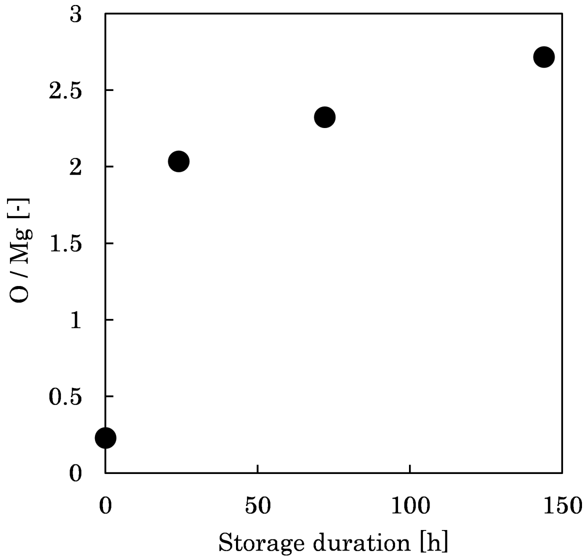

Figure 5 Variation of the ratio of O/Mg atoms.

/Mg mixture.

Acknowledgments

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