Research paper

Thermal properties of chemicals in fireworks measured with microcalorimetry

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Abstract

The blinker firework star called "kirakira-boshi" is composed of metals and antimony trisulfide (Sb_2S_3). In the manufacturing process, water is mixed with the composition. Using Mg and/or Magnesium-Aluminum alloy (MgAl) as the metal component can be a problem since their reactions are exothermic. We first analyzed distilled water and the water samples used in the manufacturing process using HPLC, and then we analyzed the water samples dispersed with Sb_2S_3. The results show that each water sample contains different anion groups.

We also performed microcalorimetric studies on the Mg-H_2O and Mg-Sb_2S_3-H_2O systems using the C-80 calorimeter of membrane mixing vessel at different temperature levels. An immediate exothermic reaction was observed when water was dropped on the Mg-H_2O system, but stopped soon after because the reaction was limited to the surface of the powder. On the other hand, when water was dropped on the Mg-Sb_2S_3-H_2O system, the reaction continued for a long time, producing Mg $(OH)_2$ and H_2S.

Potassium dichromate ($K_2Cr_2O_7$) is usually used to inhibit the reaction of a pyrotechnic containing Mg and water. In the case of the Mg-Sb_2S_3-H_2O system at 35°C, $K_2Cr_2O_7$ did not inhibit the reaction. An exothermic reaction was observed after a 6-hour induction period, which can be dangerous in an uncontrolled situation.

Keywords : fireworks, magnesium (Mg), antimony trisulfide (Sb_2S_3), potassium dichromate ($K_2Cr_2O_7$), microcalorimetry, blinker stars, exothermic reactions

1. Introduction

In general, firework stars are produced by alternately sprinkling dry fireworks composition and muddy one onto a central core. This process is repeated so many times, until a star of the desired size is produced. The manufacturing process of pyrotechnics therefore often involves the mixing of a fireworks composition and water.

A manufacturer of blinker fireworks star called "kirakira-boshi" reported me that a part of surface of the star has changed (see Figure 1). He composed star of metal(s) and antimony trisulfide (Sb_2S_3). In the manufacturing process, water (stream water near his factory) is mixed with this compound.

Magnesium reacts with water, and generates heat and hydrogen gas. Using Mg and/or MgAl as the metal component can be a problem since a tremendous amount of heat will be generated. Commonly, $K_2Cr_2O_7$ is used to inhibit the reaction. Some of the studies of Mg-H_2O system results were reported[1)2)].

Therefore, it is important to consider the stability of the metal over time for stability in storage and safety in manufacturing. No previous calorimetric studies of metal (s)-Sb_2S_3 compounds have yet been reported. This paper reports our findings on such compounds.

2. Experimental

2.1 Reagents

The reagents used were Mg powder (Kanto Metal Corporation), Sb_2S_3 powder (Fireworks factory), potassium dichromate $K_2Cr_2O_7$ (Fireworks factory), detergent containing 37% of the surface-active agent, and water from the following three sources: distilled water, water from a stream near the fireworks factory, and tap water. Each water sample was added to the detergent in a1vol. %.

2.2 Preparation of water samples

Distilled water and water samples used in the manufacturing process of fireworks were first analyzed using HPLC. The water samples with dispersed Sb_2S_3 were subsequently analyzed. As a result, the filtrate to which old realgar (As_4S_4) and Sb_2S_3 are distributed has knew the sulfate ion (SO_4^{2-}) is contained by HPLC (see Figure 2). The measurements of SO_4^{2-} and other anions (Cl^-, NO_3^-) contained in a filtrate obtained from water suspensions of old Sb_2S_3 (that had been kept for 5~20 years) and the Sb_2S_3 used in the actual experiment.

The measurements were performed as follows : 3.5 g of Sb_2S_3 was added to approximately 50 mL of distilled water. The solution was stirred and heated for 1 hour. The suspensions were stirred and heated to 70°C for 10 min. It was left to stand for 3 days and then filtered under vacuum using No.5C (see "JIS P 3801") filter paper. Distilled water was added to the 100 mL mark to obtain the analytical sample. The analytical sample was filtered through a 0.22 µm membrane filter prior to measuring. 20 µL of sample was measured with a micro syringe and the measurement was taken twice for each sample.

2.3 Preparation for the microcalorimetric studies on Mg-H_2O and Mg-Sb_2S_3-H_2O systems

The microcalorimetric studies were performed using the C-80 calorimeter (SETARAM Corporation of France) at different temperatures. For the Mg-H_2O system, Mg and water were mixed at a mole ratio of 1 : 10, whereas for the Mg-Sb_2S_3-H_2O system, Mg and Sb_2S_3 were mixed at a weight ratio of 50 : 50 and this compound added water sample. A quantity of water with a mole value ten times of Mg was added to the Mg-Sb_2S_3 composition. The measurements for both systems were carried out when the water and the sample that had been isolated by the membrane broke the membrane film (see Figure 3). In case of water sample used $K_2Cr_2O_7$, this measurement did water of either 1.2 wt.% or 5.0 wt.% of dissolved $K_2Cr_2O_7$.

3. Results

3.1 Analysis of water samples

The measurements of Cl^-, NO_3^-, and SO_4^{2-} concentrations in the water samples are shown in Table 1. The results showed no detections of Cl^-, NO_3^-, and SO_4^{2-} in distilled water. However, these ions were detected in the stream water sample from near the fireworks factory, and its concentration of NO_3^- was approximately 19 ppm.

The measurements of Cl^-, NO_3^-, and SO_4^{2-} concentrations in the filtrate from Sb_2S_3 suspensions are shown in Table 2. Cl^-, NO_3^-, and SO_4^{2-} were not detected in distilled water. However, these ions were detected in the stream water sample from near the fireworks factory. An increased concentration of SO_4^{2-}, with a maximum SO_4^{2-} concentration of 20 ppm, was detected for this sample. Cl^- and SO_4^{2-} were also detected in tap water and the stream

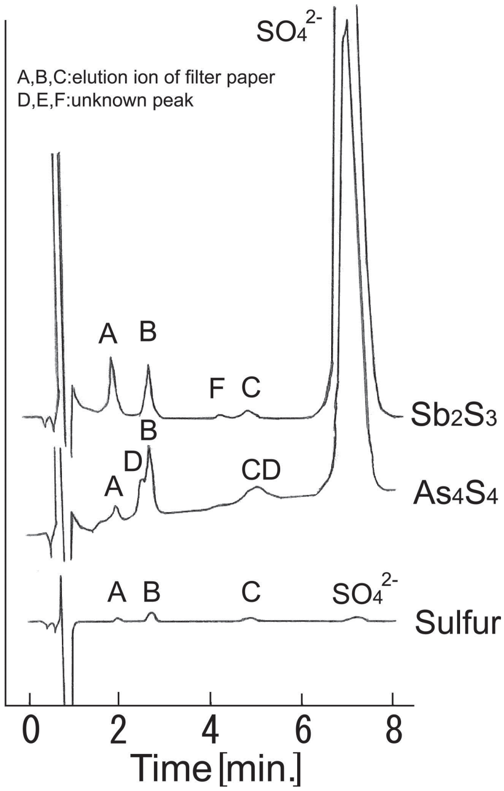


Figure 2 Water samples with dispersed sulfuric compound analyzed by HPLC.

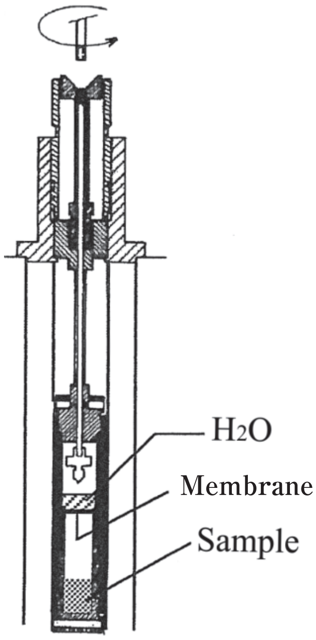
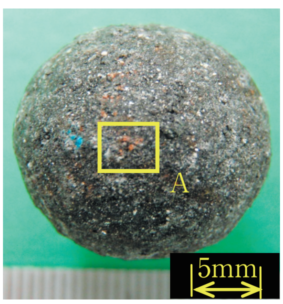
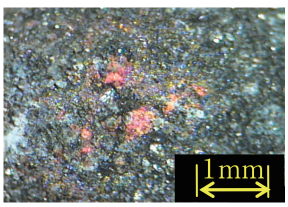


Figure 3 Membrane mixing vessel.



(a) Exterior of a star.



(b) Enlarged photo of A.

Figure 1 The blinker star.

Table 1 Concentrations of Cl^-, NO_3^-, and SO_4^{2-} in water samples by HPLC.

Sample Name	Cl^-	NO_3^-	SO_4^{2-}	pH
Distilled water*1	ND	ND	ND	6.36
Stream water near the factory	4.0	18.7	6.4	6.63
Stream water near my lab.	6.9	SQ	6.2	6.99
Tap water*1	7.3	SQ	6.7	6.81

*1 : measured only once (n=1), ND : No detection,
SQ : very small quantity (unit : ppm)

Table 2 Concentrations of Cl^-, NO_3^-, and SO_4^{2-} in the in the filtrate samples from Sb_2S_3 suspensions.

Sample Name (Sb_2S_3)	Cl^-	NO_3^-	SO_4^{2-}	pH
Fireworks factory	ND	SQ	10.8	5.58
「P-2」 by Nihon-seikou corporation	SQ	SQ	11.5	5.50
Chemical reagent	ND	SQ	8.3	5.22
Fireworks factory (another factory)	ND	SQ	20.2	4.79
Fireworks factory + stream water*2	3.9	15.7	19.4	6.71

*2 : stream water near the factory. ND : No detection,
SQ : very small quantity (unit : ppm)

water sample from near my laboratory. A maximum SO_4^{2-} concentration of 20 mM for each mol of Sb_2S_3 was detected in the filtrate obtained from a suspension of Sb_2S_3 in distilled water. Cl^-, NO_3^-, and SO_4^{2-} were detected in the filtrate obtained from a suspension of Sb_2S_3 in the stream water sample from near the fireworks factory. Only the concentration of SO_4^{2-} in the stream water sample from near the fireworks factory increased. As a result, it was found that each water sample contained different anion groups.

3.2 Microcalorimetric studies on the Mg-H_2O and Mg-Sb_2S_3 systems

The heat flow measurements for the Mg-H_2O system at a constant temperature of 35°C are shown in Figure 4. The theoretical value for the reaction enthalpy is -352.9 kJ/mol.[3] However, measurement of enthalpy toward this theoretical value of these reaction in distilled water and one containing sulfate ion are hardly 1.0% and 2.3% respectively, and it is not reactive less (see Table 3). When water was added to the Mg powder, an immediate exothermic reaction was observed. However, the reaction was short because it took place only on the surface of the powder.

The three ingredients of the Mg-Sb_2S_3-H_2O system were mixed in the test tube, and tested. When water was added to the Mg-Sb_2S_3 mixture, an odor was observed. The simplified measurement with the indicator tube was performed. 200 ppm of H_2S was generated within 10 min after water was added (see Figure 5). A less vigorous reaction was observed when distilled water was used in the Mg-Sb_2S_3-H_2O system.

The rates of heat flow over time when distilled water and stream water were used in the Mg-Sb_2S_3-H_2O system are shown in Figures 6 and 7, respectively. Heat was generated again in approximately 6 hours, and the reaction continued for a long time while producing Mg$(OH)_2$ and H_2S. Analysis of the product showed that Mg powder was converted entirely to Mg$(OH)_2$ at the end of the reaction. The reaction was more exothermic when stream water near the fireworks factory was used instead of distilled water as indicated by the higher heat generation rate. The heat generation rate for this reaction

Table 3 Result of Mg-H_2O system by C-80.

	Enthalpy (kJ/mol)	Reaction of rate (%)
Distilled water	−3.4	1.0
Sulfate ion	−8.2	2.3

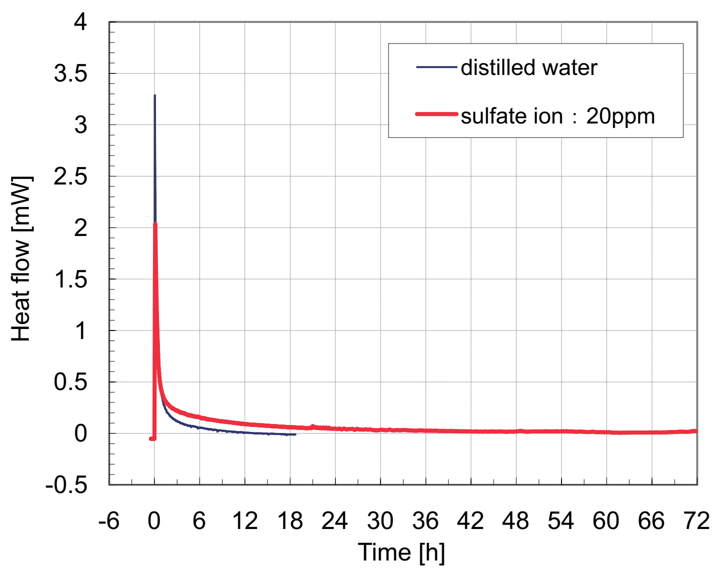


Figure 4 Rate of heat flow over time for the Mg-H_2O system.

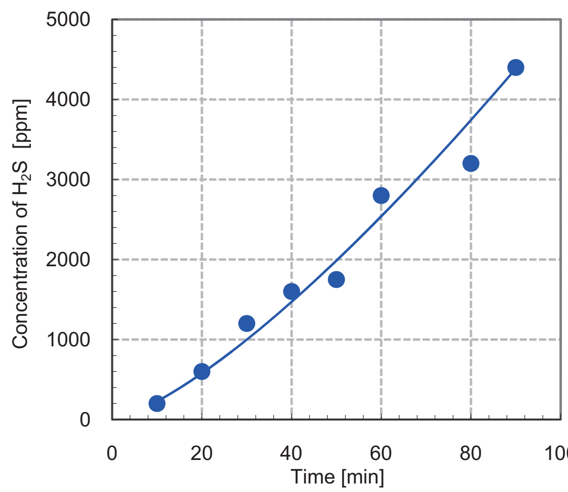


Figure 5 Concentration of H_2S over time for the Mg-Sb_2S_3 system at 65°C.

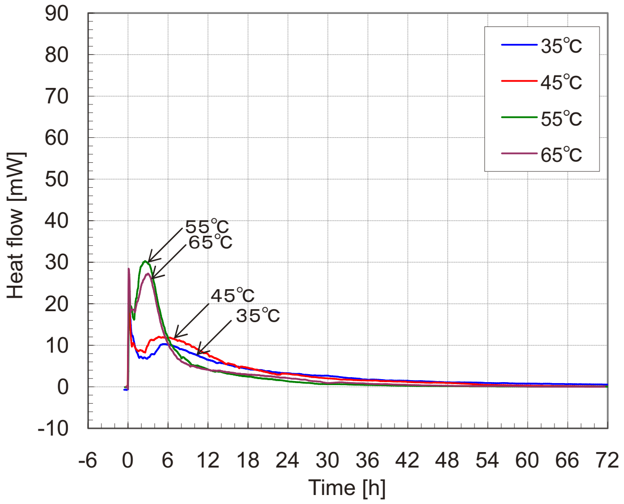


Figure 6 Rate of heat flow over time for the Mg-Sb_2S_3-H_2O (distilled water) system.

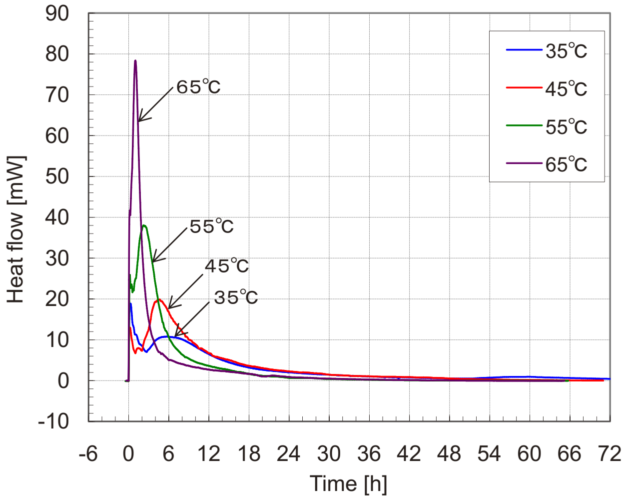


Figure 7 Rate of heat flow over time for the Mg-Sb_2S_3-H_2O (stream water) system.

varied with the surrounding temperature.

The effect of $K_2Cr_2O_7$ on Mg-Sb_2S_3 and Mg-Sb_2S_3-H_2O systems were also examined. The reaction enthalpies were measured by adding stream water containing $K_2Cr_2O_7$ to the system. This rate of flow heat is shown in Figure 8. An induction period with no heat generation was observed at 35°C. Heat was then suddenly generated after 6 hours, which can be dangerous in an uncontrolled situation. No such induction period was observed at approximately 45°C or more. The system immediately reacted with water at 65°C and higher, leading to a steep increase in the rate of heat generation.

5. Conclusions

In the analysis of water samples, the types of anions

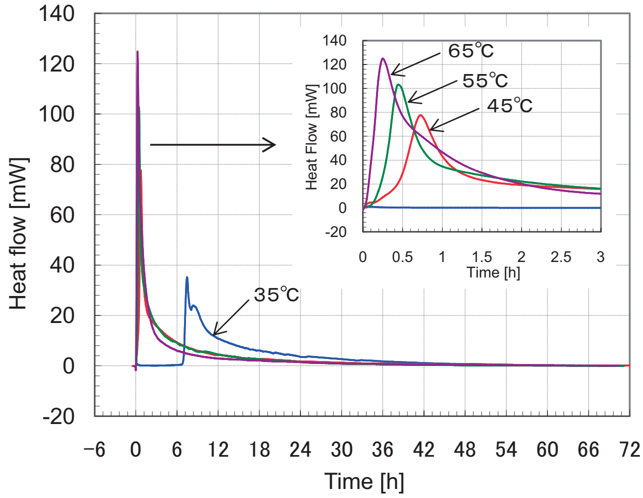


Figure 8 Rate of heat flow over time for the Mg-Sb_2S_3-H_2O (stream water) system with $K_2Cr_2O_7$ (1.2wt.%).

contained in natural water and tap water such as the stream water are different. A maximum SO_4^{2-} concentration of 20 mM for each mol of Sb_2S_3 was detected in the filtrate obtained from a suspension of Sb_2S_3 in distilled water. The filtrate obtained from a suspension of Sb_2S_3 in stream water of the fireworks factory showed an increased SO_4^{2-} concentration.

In the microcalorimetric studies of Mg-H_2O and Mg-Sb_2S_3-H_2O systems, an exothermic reaction was observed as soon as water was added to the systems. However, the reaction occurred only on the surface for the Mg-H_2O system. Heat was generated again after approximately 6 hours while producing Mg $(OH)_2$ and H_2S for the Mg-Sb_2S_3-H_2O system. An induction period with no heat generation was observed in the Mg-Sb_2S_3-H_2O system when water containing 1.2 wt% of $K_2Cr_2O_7$ was added at 35°C, which can be dangerous in an uncontrolled situation. The rate of heat generation increased when distilled water was added.

It is important to note that if water containing $K_2Cr_2O_7$ is added to this system, heat will be generated in a short time.

6. References

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微小熱量計を用いた煙火組成物の混触反応による熱特性

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「キラキラ星」と呼ばれる星は，金属―三硫化アンチモン系の点滅剤が使用され，その製造工程は，水を使って作られている。しかし，この系において，金属にMgまたはMgAl使用した場合，化学変化を起こし，問題となっている。

そこでまず，製造工程で使用する水とSb_2S_3-H_2O系について液体クロマト分析を行った。

その結果，天然水(沢水)や水道水など使用する水によって含まれる陰イオンが異なることが分かった。また，水にSb_2S_3を分散させた濾液は，硫酸イオン濃度が増加していた。

次にC-80熱量計のメンブレン混合容器を用いて，混触反応について調べ，初めにMg-H_2O系の発熱量の測定を行った。Mg-H_2O二成分系では，水を滴下した直後から発熱反応を生じるが，その反応は表面のみですぐ止まった。

Mg-Sb_2S_3-H_2O三成分系では，水を滴下した直後に発熱を開始し，$Mg(OH)_2$と硫化水素を発生しながら発熱反応が進み，Mg金属はすべて$Mg(OH)_2$となった。

従来，Mgと水との反応を抑えるために，$K_2Cr_2O_7$が使用されている。しかし，Mg-Sb_2S_3混合物に$K_2Cr_2O_7$を含んだ水を滴下した場合，35℃では発熱をしない誘導期が存在し，その後，突然発熱反応が起こる。つまり，管理されていない状況下で発熱反応が起こる可能性がある。45℃以上では，滴下してすぐに発熱し，誘導期は見られなくなる。蒸留水のみを滴下した場合より，$K_2Cr_2O_7$を含んだ水を使用した場合の方が熱発生速度は大きくなった。

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