Research paper

Characteristics of heat flow of magnesium particles measured with high sensitivity calorimeter

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Abstract

Magnesium alloy is used as a material of the container of a personal computer and a cellular phone. Magnesium plays an important role in the field of the chemical synthesis as a raw material of an organic metal agent. However, the magnesium powder is involved in a fire and a dust explosion. In addition, it prevents the fire fighting in the magnesium fire because there is the possibility that it easily reacts with water and generates heat and hydrogen.

The characteristics of heat flow of magnesium particles were investigated with a thermal activity monitor (TAM Ⅲ) which was the high sensibility calorimeter. The measurement periods of most tests were several days. The particle size of magnesium powder of 99.6 wt % was below 150 μm. The TAM Ⅲ demonstrated the heat flow increased in air, argon and nitrogen atmosphere when the magnesium powder was used as the sample. The heat flow was almost constant in various atmospheres when the magnesium turnings were used as the sample. It was elucidated the increase of heat flow had the relation with the surface area of magnesium particles. The reaction of magnesium with water was examined by the TAM Ⅲ. The heat flow with the addition of water was approximately ten times larger than the heat flow without the addition of water.

Keywords: Magnesium powder, Small heat release, High sensitive calorimeter.

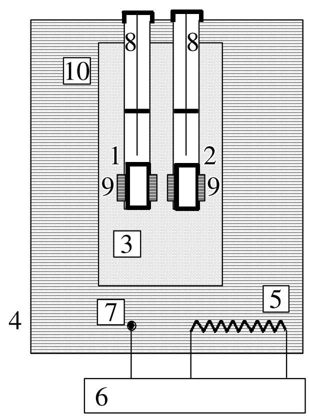
1. Introduction

Magnesium alloy is used as a material of the container of a personal computer and a cellular phone. Magnesium plays an important role as a raw material of an organometallic reagent in the field of the organic synthesis. However, the magnesium powder might frequently become the cause material of fire. Moreover, there is the possibility that it easily reacts with water and generates heat and hydrogen. It might become the inhibitor of the fire fighting.

The behavior of small heat generation of the magnesium powder was examined in the present study with a high sensitivity calorimeter (TAM Ⅲ). In addition, when water was added to magnesium, the influence on the generation of heat was investigated.

2. Experimental

Figure 1 shows the outline of TAM Ⅲ apparatus which is the high sensitivity calorimeter. It has a reference vessel and a sample vessel of the 20 ml and 4 ml. It can measure heat flow from nW to mW order occurred from sample under the isothermal condition because its baseline is very stable. Table 1 shows the experimental conditions of the ambient temperature, the sample amount and the volume of water and so on. In addition, the heat of reaction measured is shown in Table 1. The purity of nitrogen and argon is 99.9 vol % or more.



1: reference vessel
2: sample vessel
3: block
4: oil bath
5: heater
6: temperature controller
7: temperature sensor
8: lift bar for vessel
9: heat flux meter
10: measurement unit

Fig. 1 Outline of TAM Ⅲ.

Table 1 Experiment condition .

No.	sample vessel volume (ml)	sample mass (g)	temperature (°C)	atmosphere	heat of reaction ($J \cdot g^{-1}$) first period	second period	total
1	20	1.00	50	Air	0.23	0.23	0.46
2	20	1.00	50	Air	0.66	0.71	1.37
3	20	1.00	65	N_2	2.11	1.96	4.07
4	20	1.00	65	Air	2.09	2.23	4.32
5	20	1.00	50	N_2	2.15	2.54	4.69
6	20	1.00	65	Air	4.56	4.47	9.03
7	20	1.00	50	Air	0	0	0
8	20	1.00	50	Air	0	0	0
9	4	0.20	65	Air	3.46	1.19	4.65
10	4	0.40	65	Air	3.32	0.98	4.30
11	4	0.20	50	Air	2.07	1.17	3.24
12	4	0.20	65	Air	3.22	1.22	4.44
13	20	1.00	65	Air	—	—	908.34

Sample form of No. 7 and No. 8 was turnings. Sample form except for No. 7 and No. 8 was powder.
Test of No. 13 was the experiment of addition of water. Added water amount was 18 wt%.
First period: regarding to 20 ml vessel: 2 hr – 26 hr
Second period regarding to 20 ml vessel: 26 hr – 50 hr
First period regarding to 4 ml vessel: 12 hr – 36 hr
Second period regarding to 4 ml vessel: 36 hr – 60 hr

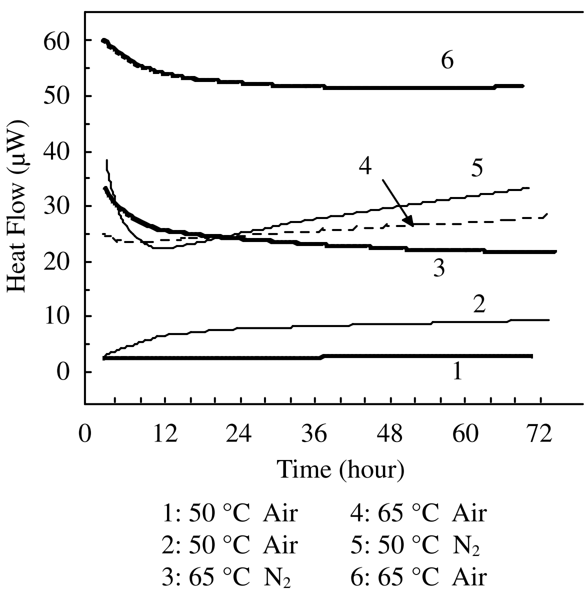


Fig. 2 Heat flow of magnesium powder in various conditions measured with 20 ml vessels.

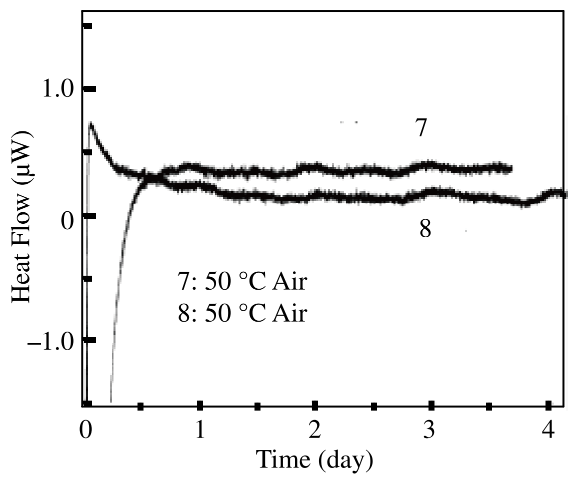


Fig. 3 Heat flow of magnesium turnings measured with 20 ml vessels.

The magnesium powder and magnesium turnings were used as a sample. Aluminum oxide (Al_2O_3) was used as the standard sample. The purity of magnesium powder and magnesium turnings was 99.9 %, and 98 %, respectively. The magnesium turnings were dried after they were washed with acetone and ethanol. The particle diameter of magnesium powder 99.6 wt% was less than 0.150 mm (–100 mesh) regarding to all particles. Averaged magnesium turning was 10 mm in length, and 1 mm in width, and 0.4 mm in thickness approximately.

The volume of sample vessels was 20 ml and 4 ml. The sample vessel was made of stainless steel. The sample mass was 1.0 g in the 20 ml vessel tests. The sample mass was 0.20 g and 0.40 g in the 4 ml vessel tests. The sample was put in the sample vessel and weighted. Distilled water was used for the water addition test. Added water amount was 18 wt%.

After the air in the sample vessel was removed with a rotary pump, argon or nitrogen was introduced into the sample vessel. The space inside sample vessel is enough for magnesium to react with the gas during the measurement.

The empty reference vessel was used in the 20 ml sample vessel tests. The reference vessel packed with Al_2O_3 of which was heat capacity was almost the same as that of the magnesium sample in the 4 ml sample vessel tests.

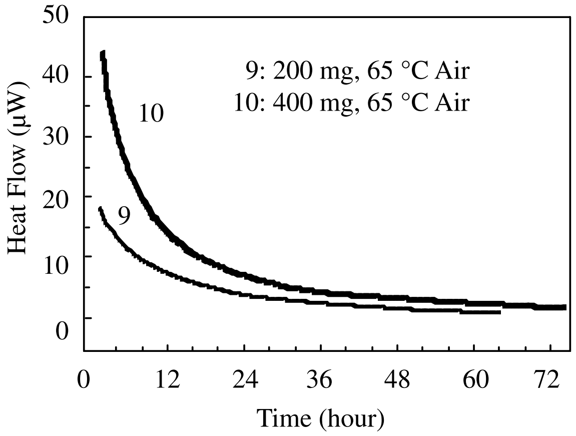


Fig. 4 Heat flow of magnesium powder in two amount of sample measured with 4 ml vessels.

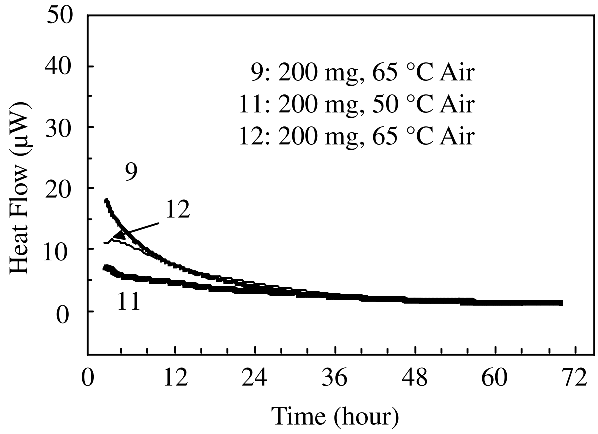


Fig. 5 Heat flow of magnesium powder in two temperatures measured with 4 ml vessels.

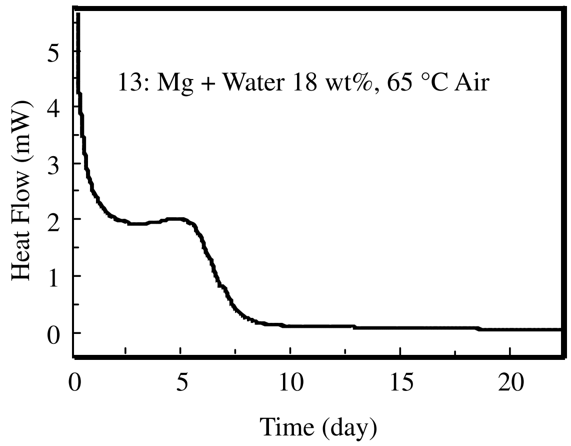


Fig. 6 Heat flow of magnesium powder added with water measured with 20 ml vessels.

After Al_2O_3 was heated under air, it was used in the 4 ml vessel tests as the reference material. Its exothermic heat flow was zero approximately in the TAM III measurements.

It takes about two hours and twelve hours until the heat balance stabilizes in the case of the 4 ml and 20 ml vessel tests respectively when the vessels were set up in the apparatus. The 4 ml vessel test is more sensitive and better stability than that of the 20 ml vessel tests. Because the more sample amount can be used in the 20 ml vessel tests, the scale effect can be investigated.

3. Results and discussion

The heat flow results in various experimental conditions are shown in Fig. 2 - 6. The horizontal axis shows the elapsed time. The vertical axis shows heat flow from the sample. The number in Figures corresponds to the experiment number of Table 1.

Figure 2 shows the time history of heat flow of magnesium powder in the 20 ml vessel. The experiments were conducted under various atmosphere conditions. The heat generation from magnesium powder was detected under the air, the nitrogen and the argon atmosphere with the similar tendency in the 20 ml vessel tests. The heat flow increased with the elapsed time in some tests of the 20 ml vessel tests. The heat flow difference by each atmosphere was within a range of the measurement error. The heat of generation of magnesium powder of No. 1 in two days without added water was 0.46 $J \cdot g^{-1}$.

Figure 3 shows the time history of heat flow of magnesium turnings in the 20 ml vessel. The generation of heat was not detected for the magnesium turnings under the air, the nitrogen and the argon atmosphere. When the surface area of the magnesium sample was small, the generation of heat was undetectable. The generation of heat happened because of the surface reaction of magnesium when the results of magnesium powder were considered [1]. The change of the crystallographic structure on the magnesium surface was presumed.

Figure 4 shows the time history of heat flow of magnesium powder in the 4 ml vessel when the sample mass of 0.20 g and 0.40 g was applied to the measurements. When the amount of magnesium increased from 0.20 g to 0.40 g in the 4 ml vessel, the heat flow increased with the sample amount. This result was appropriate considering the increase of the surface area.

Figure 5 shows the time history of heat flow of magnesium powder in the 20 ml and 4 ml vessel in 50 °C and 65 °C of ambient temperature. Though the ambient temperature was raised from 50 °C to 65 °C , the significant difference was not observed. This result suggested heat flow was due to the surface reaction not the reaction of the gas molecular because the gas molecular reaction depended on the temperature.

The heat generation was detected but did not increase in the 4 ml vessel while the heat flow increased in some of 20 ml vessel tests. This result that the heat flow did not increase in the 4 ml vessel tests was similar to the other report with the example of measuring magnesium powder by TAM2277 [2]. The heat flow of Ref. 2 was smaller than the results of this paper because the particle size with 0.2 mm was used in Ref. 2.

Figure 6 shows heat flow increases when water is added to magnesium powder under air. The heat flow with the added water to the powder was ten times lager than the magnesium powder without the added water. It was elucidated that the magnesium powder reacted with water because the heat flow increased and decreased after when the water addition. The heat of reaction with Magnesium and water was 908.3 J · g^{-1}. The heat of reaction of Calcium with water was 7.34 kJ · g^{-1} [3]. That of Magnesium was very small with compared with that of Calcium.

4. Conclusions

The small generation of heat behavior of the magnesium powder was examined with a high sensitive calorimeter. The influence of the added water on the thermal behavior was investigated. The following conclusions were obtained.

(1) Magnesium powder generates heat in various atmospheres. It was suggested that the magnesium surface was the cause of heat generation.

(2) When the amount of magnesium increased from 0.20 g to 0.40 g in the 4 ml vessel, the heat flow increased with the sample amount.

(3) Though the ambient temperature was raised from 50 °C to 65 °C, heat flow did not vary largely.

(4) The generation of heat flow after the water addition was ten times lager than the magnesium powder without the added water.

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