Technical know-how in thermal analysis measurement

—How the effects of measurement condition influence the results—

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1. Introduction

Since thermal analysis measurement is easy to be performed, anyone can obtain the same measurement result on a pre-determined measurement condition. For this reason, the use of thermal analysis is applied among analytical techniques not only in research and development but also in quality control. However, since the measurement result in thermal analysis largely depends on the measurement condition, selecting the most appropriate measurement condition with regards to the sample is important.

2. Considerable effects on the measurement result derived from the measurement condition

2.1. Sample shape

The influence on the sample shape is largely divided into two types. First, the influence on the peak sensitivity obtained such as in DTA (Differential Thermal Analysis) or DSC (Differential Scanning Calorimetry). The DTA and DSC sensor (thermocouple) are attached on the under side of the sample stage on which the sample pan containing the sample is mounted. Thus, the transfer of heat from the sample to the thermocouple is influenced by the condition of the contact surface between the sample itself and the bottom of the sample pan, as well as its degree of adhesion. Ideally, it is desirable that the sample extensively adheres to the large surface area on the bottom of the sample pan, thus, crimp pan is commonly used in DSC measurement.

Second, the progress of a reaction depends on the shape of the sample. A common example is the oxidation reaction resulting from the reaction between oxygen and the sample surface that is exposed to oxygen. For this reason, the amount of oxidation reaction varies with the size of available surface area. The amount of oxidation reaction with a powder sample is larger than that of a block type sample because the surface area available for oxidation in the powder sample, which consists of many sample particles, is always larger than that of the block type sample. Therefore it is essential to take note on the particle diameter as well as the particle size distribution of the sample. Also, how the evolved gases are released from the sample thru decomposition reaction varies with the shape and particle size of the sample.

2.2. Amount of sample

As the amount of sample increases, the peak temperature as well as the reaction temperature of the mass change shifts to the high temperature. This is mainly caused by three main factors namely, first, there is a large temperature distribution within the sample; second, there is a large temperature difference between the sensor and the sample; and third, the temperature changes during the course of reaction in the constant rate heating measurement. On the contrary, if the sample amount is small, the amount of mass change as well as the peak area decreases making it difficult in confirming the mass change. Usually, it is desirable to decrease the amount of sample in order to increase the resolution. On the contrary, in order to confirm minute changes, it is recommended to increase the amount of sample so as to enhance the observable changes.

2.3. Heating rate

The peak temperature and the mass change shifts to a higher temperature as the heating rate increases. Decreasing the heating rate leads to an increase in the resolution. On the other hand, it is desirable to increase the heating rate in order to increase the sensitivity.

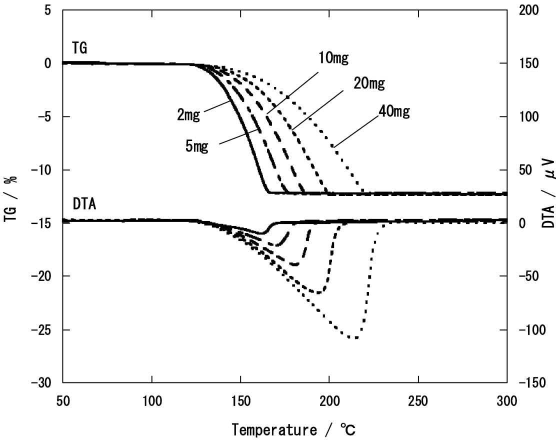

Fig. 1. The effect of sample amount on the result. Sample: calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$), sample amount: 2–40 mg, heating rate: 10 K/min. The peak and mass change temperature shifts to high temperature as the sample amount increases but mass loss percentage does not change. However, because the amount of sample differs, the mass loss value also differs. The DTA peak area increases as the sample amount increases.

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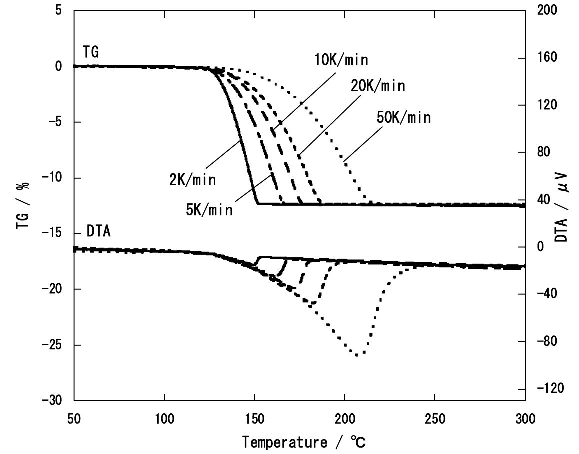

Fig. 2. The effect of heating rate on the result. Sample: calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$), amount of sample: 5 mg, heating rate: 2–50 K/min. The peak and mass change temperature shifts to high temperature as the heating rate increases but the mass loss percentage does not change. The DTA peak area remains the same with regards to time but if the X axis is changed to temperature, the peaks become larger in relation to heating rate.

2.4. Sample pan

2.4.1. Sample pan material

The temperature range as well as the sample's reactivity must be taken into consideration in selecting a sample pan. The most commonly used is the Al sample pan and since the melting point of Al is 660°C, using the Al pan at near melting point can cause damage to the instrument which is hazardous. The Pt pan (~1500°C) is commonly used in measurements above the melting point of Al. However, depending on the sample, Pt may act as a catalyst, causing possible reactions with the sample. Precautionary measures must be considered in measuring metal samples because the formation of alloy is highly possible. If the sample reacts with Pt, the use of pans with low reactivity such as SiO_2 (~1000°C) or Al_2O_3 (~1500°C) is recommended. But because the thermal conductivity is lower compared to the metal sample pans, the detection ability of DTA and DSC also decreases.

◆ Method of confirming the reactivity of the sample with Pt

The sensitivity of DTA in Pt pan is high. However, there is a possibility of causing damage to the instrument if the sample reacts with Pt. For this reason, it is necessary to assess the reactivity of the sample with the Pt pan in measuring unknown samples. For example, place a chip (portion) of Pt pan on the base of the Al_2O_3 pan and mount the sample on top of it. By confirming the Pt after measurement, then we can acquire an understanding on the reactivity of the sample with Pt. Even if the sample reacted with Pt, it will not cause any damage to the instrument because the reaction occurred inside the Al_2O_3 pan.

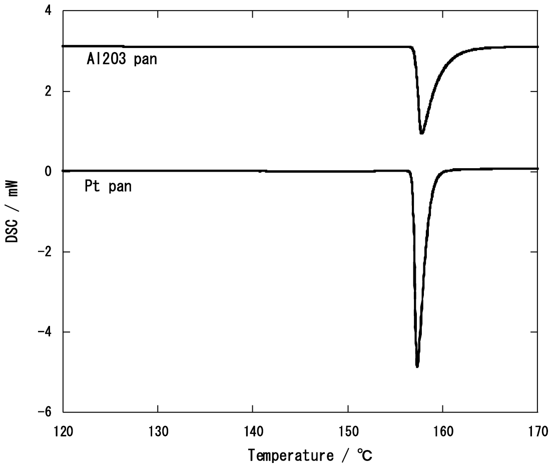

Fig. 3. Difference between Pt pan and Al_2O_3 pan. Sample: In, amount of sample: 1 mg, heating rate: 10 K/min. The reaction peak intensity in Pt pan is higher than Al_2O_3.

2.4.2. Forms of sample pans

Since most TG-DTA measurements measure the decomposition reaction, most measurements use open pan for a smoother release of evolved gases outside the system. The sample pan and its degree of contact should be considered, thus crimp pan is commonly used in DSC measurement. Also, if volatilization or dehydration has to be suppressed, the sealed pan is used. In addition, using the sealed pan with a pin-hole on the lid is effective in measuring the effect of partial pressure of evolved gases.

2.5. Measurement atmosphere

The measurement atmosphere, mainly air atmosphere or inert gas, can be selected depending on the objective of the measurement. Specifically, in measurements such as oxidation or combustion where oxygen in the atmosphere is necessary, air atmosphere is employed. On the other hand, inert gas atmosphere is used in measurements where oxidation is unnecessary or in decomposition reaction measurements. In order that the atmospheric gas will have an effect to the sample's reaction, selecting a gas corresponding to the objective of the sample's reaction is important. In TG-DTA, it is necessary that the atmospheric gas flows at a constant flow rate during measurement. This is to reduce the effect of vapor pressure by an on-going reaction of gas decomposition, thus the evolved gases are quickly eliminated from the furnace. It is important that these evolved gases are not retained in the furnace because gases may cause an adverse effect on the instrument. The flow rate in usual TG-DTA measurement is several 100 m*l*/min. While in DSC measurements, to prevent the loss of heat outside the system by the atmospheric gas, most measurements use static air or flow rates of several 10 m*l*/min.

◆ The tendency for oxidation and combustion under an inert gas atmosphere

(1) Is the concentration of the residual oxygen high?

Even in measurements under inert gas atmosphere, the oxygen concentration cannot be eliminated and residual oxygen always exists. In measuring highly oxidizing material, as much as possible, the oxygen concentration inside the instrument must be decreased. During sample setting, the furnace is exposed to ambient atmosphere. After setting the sample, purge the sample thoroughly to reduce the residual oxygen in the sample's periphery. Longer purge time will usually decrease the residual oxygen but in some cases, it is not sufficiently effective. Especially in TG-DTA measurements, optimizing the inlet, the gas flow method of the carrier gas or the flow rate will change the concentration of residual oxygen. The usual gas flow is from G3 (posterior region of the balance), as shown in Fig. 4, purging at 1000 m*l*/min, then the flow rate is changed depending on the objective, prior to measurement (for horizontal type, 1000 m*l*/min is effective). Although vacuum displacement is also effective but the necessity of a vacuum pump, displacement operation, connection or such attachment becomes complicated and still sufficient effect is unobtainable. Recently, by using the gas flow unit (option) purging is effectively accomplished in a simple and brief way (~10 minutes), lowering the residual oxygen concentration (<20 ppm).

(2) Possible reactions with N_2 gas

In some cases, it is apparently believed that oxidation reaction in metals and metallic compounds can be confirmed under N_2 gas atmosphere. Depending on the sample, N_2 gas may generate nitride; in this case, Ar gas is used for confirmation. Since Ar gas is an inert gas, it does not generate compounds.

(3) Evolution of oxygen from the sample

In materials such as resin, we can confirm very few exothermic peaks and mass losses in some cases. Because the oxygen, evolved as decomposition product generated from the sample, will react with the sample again, thus it is essential to study the decomposition behavior of a material in detail or perform evolved gas analysis.

(4) Unrelated reactions occurring the with atmosphere

If the observed exothermic peak and the mass loss obtained from air atmosphere and inert gas atmosphere have the same size, then there is no difference in the peak area as well as the mass loss ratio. Viewing this as non-atmosphere related reaction is important. Usually, an exothermic peak associated with mass loss is evaluated as combustion; others include exothermic hardening with simultaneous evolution of gases. But in some cases of structural transition such as in crystallization or crystal transition, the gases trapped within the sample are evolved. Also, in reactions such as cyclic polymerization, in which an exothermic peak associated with evolved gases occur, even if the atmosphere is changed and still no difference is observed, then the reaction is a non-atmosphere related. Ideally, it is desirable to analyze the specific details of a reaction using the combination of other analytical instruments.

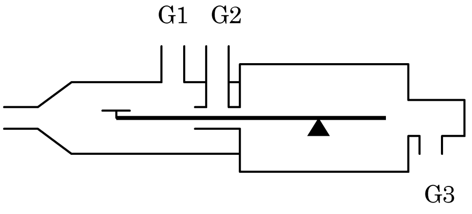

Fig. 4. Structural diagram of TG8120.

3. Case studies

3.1. The effect of humidity in atmosphere

Although the difference between air and inert gas atmosphere was mentioned in the condition dependence in "2.5 Atmosphere" (pros and cons of a sample and its reaction depending on its gas type), strictly there is one more important difference.

In air atmosphere, the room air is often supplied through an air pump to the module. On the other hand, in inert gas atmosphere, the atmospheric gas is supplied using a gas cylinder which differs in atmospheric gas humidity. Naturally, atmospheric humidity is present in the room air while gas cylinders have a dry atmosphere. Because the water's partial pressure affects the humidity, it affects the dehydration behavior.

Figure 5 shows the comparison of TG and DTG (Differential Thermo Gravimetry) curve of gypsum dihydrate in air (through an air pump) atmosphere and N_2 (N_2 gas cylinder) atmosphere. Although a dehydration reaction of gypsum dihydrate has occurred at 100°C, the reaction in N_2 atmosphere was observed in slightly lower temperature than in air atmosphere. The dehydration reaction is not related with the absence or presence of oxygen. But, it is affected by the humidity.

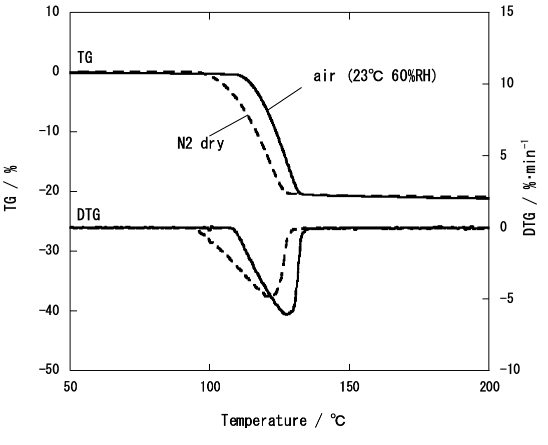

Fig. 5. Differences in using an air pump and an N_2 gas. Sample: $CaSO_4 \cdot 2H_2O$; sample amount: 5 mg; heating rate: 5 K/min. The dehydration occurred in the low temperature when using the dry N_2 gas from the gas cylinder.

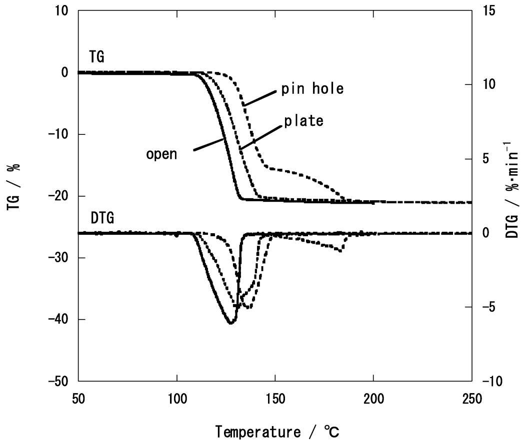

Fig. 6. The effects of the sample pan form. Sample: $CaSO_4 \cdot 2H_2O$; sample amount: 5 mg; heating rate: 5 K/min. The water vapor partial pressure of the sample's periphery is different because the dehydration reaction is influenced by the sample pan form.

High humidity suppresses the progress of a reaction, thus reaction temperature shifts to a higher temperature. For this reason, the reaction progresses at a lower temperature when using the dry N_2 gas atmosphere; and on the contrary, the reaction occurs at a higher temperature when using the atmosphere at room humidity.

3.2. The influence of self-generated atmosphere on the sample

The gases evolved from the sample will also influence the reaction. In the evolved gas reaction, it is important to consider the partial pressure in the sample's periphery. For this reason, most measurements in TG-DTA use an open pan with a gas flowing to decrease the partial pressure effect of the evolved gases from the sample; and to immediately eliminate the evolved gases, preventing the effect of self-generated atmosphere. On the contrary, using the self-generated atmosphere in a measurement can possibly increase the resolution of the measurement result.

Figure 6 shows the TG and DTG result of gypsum dihydrate using 3 different sample pans namely an open pan, a pan with an Al plate and a pin-hole sealed pan. The open pan showed a single phase of mass loss while a two-phase mass loss was confirmed in the pin-hole sealed pan. The sample pan with an Al plate was found in between the two samples but a shoulder was observed in the DTG curve. These are the effects of self-generated atmosphere. The dehydration process of gypsum dihydrate is shown below.

① $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2\,H_2O + 3/2\,H_2O$

② $CaSO_4 \cdot 1/2\,H_2O \rightarrow CaSO_4 + 1/2\,H_2O$

First, 3/2 molecules of the water in gypsum dihydrate was dehydrated and gypsum hemihydrate was derived, further dehydration occurred and an anhydrite was formed. The two-phase dehydration reaction in gypsum dihydrate occurs in this manner. When the reaction progresses, the water vapor partial pressure will decrease and the 2 reactions occur continuously. On the other hand, only a single phase weight loss is observed in using an open pan because the evolved gases are rapidly eliminated from the system.

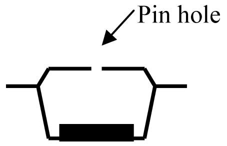

Fig. 7. Pin-hole sealed pan.

However, because the evolved gases are being desorbed from the pin hole in the pin-hole sealed pan, the water vapor partial pressure in the sample's periphery has extremely increased, inhibiting the dehydration reaction. In this time, if the shift width of the dehydration temperature is different in the two dehydration reactions, then those reactions will be separated. With this result, we can discuss in detail the respective reactions. In this example, because the shift of the dehydration temperature is larger in ② than in ①, due to the effect of the partial pressure of water vapor, the dehydration temperature in ② has remarkably shifted to a higher temperature which can be confirmed as a 2-phase weight loss. Also in comparing the open pan and the sample pan with Al plate, since dehydration was suppressed, a slight effect is obvious.

As stated above, the continuous formation of a dehydration reaction as such can be separated by using the pin-hole sealed pan. In some cases, it is also possible that a different reaction is observed when using the self-generated atmosphere.

◆ Pin-hole sealed pan

A pin-hole sealed pan is a fully sealed Al pan with a pin hole on the lid. Since the evolved gases from the sample are being released through the pin hole, then the partial pressure of the evolved gases inside the pan increases.

4. Conclusion

In thermal analysis, the effect based on the measurement condition dependence has been described. By changing the measurement condition and by considering its dependence, it is possible to obtain an effective result. Nowadays, in the atmosphere of controlled humidity such as high water vapor concentration in thermal analysis (humidity controlled thermal analysis) is strongly being carried out. It is possible to measure the effects of water vapor on the thermal degradation of a material. The amount of sample, heating rate and such conditions affect the reaction rate; and by using the sample reaction rate controlled TG (Dynamic TG), additional findings can be possibly obtained, such as the effect of self-generated atmosphere.