Design of A New Differential Scanning Calorimeter

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Abstract. The core component of DSC is a temperature difference sensor used to measure the temperature change of sample and reference material during reaction. Taking temperature difference sensor as the research object, a new DSC is designed, which uses many pairs of thermocouples in series to form a radiating thermocouple stack to improve the calorimetric sensitivity of the temperature difference sensor and reduce the measurement error caused by the uneven temperature distribution on the sensor. Through theoretical analysis, it can be seen that the original signal acquisition volume of the temperature difference sensor with multiple pairs of thermocouples has increased greatly, the calorimetric sensitivity is higher, and the error is smaller. Based on the finite element analysis software ANSYS, the steady state thermal analysis is performed on the high-sensitivity temperature difference sensor and the dumbbell-type temperature difference sensor respectively. The results show that the temperature difference of the high-sensitivity temperature difference sensor is 40.8% ~ 52.3% lower than that of the dumbbell-type temperature difference sensor under different working temperatures, which greatly reduces the measurement error caused by the uneven temperature distribution.

1. Introduction
Differential scanning calorimeter (DSC) is a thermal analysis instrument used to measure the energy difference (or power difference) and temperature relationship between the sample to be tested and the reference under program-controlled temperature and a certain atmosphere, because of its simple operation, high sensitivity and resolution, low sample consumption and good repeatability, it has been widely used in various fields such as petroleum, chemical industry, metallurgy, biopharmaceutical and so on[1-2]. When performing thermal analysis with a differential scanning calorimeter, the sample used for measurement is only a few milligrams, so the heat flow in and out of the sample which represents the endothermic or exothermic process is generally milliwatt or even microwatt[3]. To accurately detect such a weak signal, it is necessary to use a high-sensitivity temperature difference sensor. In this paper, by increasing the number of thermocouples, improving the material of thermocouples and the structural shape of the sensor, the calorimetric sensitivity of the calorimeter is improved, and the measurement error caused by the uneven temperature distribution on the sensor is reduced.

2. Basic principle of DSC
According to different measurement methods, DSC can be generally divided into two types: power compensation DSC and heat flow DSC[4]. The curve generated by measurement is called DSC curve. DSC curve takes the rate of heat change of the sample as ordinate and takes the time or temperature as abscissa. It can quantitatively analyze the process of heat change caused by physical or chemical changes in the sample.
2.1. Principle of heat flow DSC
The sample and the reference material of heat flow DSC are heated in the same heating furnace at the same power, and then, the temperature difference between the sample and the reference material is measured by the temperature difference sensor. According to heat flow equation, it is converted into the heat flow difference and output in the form of DSC curve.

2.2. Principle of power compensation DSC
The sample and reference material of power compensation DSC have independent heater and sensor respectively, and the whole system is controlled by two temperature control systems. One of the temperature control systems controls the heating and cooling of the sample and the reference material according to the rate set by the system[5], the other system is used to compensate the temperature difference caused by the exothermic or endothermic of the sample, so that the sample and the reference material always maintain the same temperature. The endothermic or exothermic rate of the sample can be calculated by measuring the power difference compensated by the power compensation unit.

3. Design of new calorimeter
3.1. Structure and operation principle of calorimeter
The new DSC designed in this paper belongs to heat flow DSC, as shown in figure 1, it is mainly composed of main engine, heating furnace, data processing system, amplifier, differentiator, program temperature controller, gas flow control system, computer, printer and other components. The furnace body is heated or cooled at a certain rate through temperature control system. When the temperature changes uniformly, the sample will absorb or release heat due to chemical changes, which will cause temperature difference between the sample and the reference material, a temperature difference sensor is installed under the crucible of the sample and the reference substance. The temperature difference sensor captures the signal and transmits it to the signal amplifier, the signal amplifier amplifies the original signal and transmits it to the A/D converter. The A/D converter converts analog signal into digital signal that can be recognized by the computer and then outputs it to the computer. The calculator processes the signal and generates the DSC curve. During the operation of the calorimeter, the gas flow control system controls the type and inflow of gas to provide the gas environment required for the reaction.

![Figure 1. Composition of heat flow DSC system.](image1)

![Figure 2. Dumbbell-type sensor.](image2)

3.2. Improved design of temperature difference sensor
The core component of DSC is the temperature difference sensor which is used to capture the temperature difference signal. At present, a pair of thermocouples are usually made into dumbbell shape by the temperature difference sensor used in domestic calorimeter, as shown in figure 2, and its material is constantan alloy. On the one hand, the sensor carries the crucible of sample and reference material, on the other hand, it uses the thermoelectric property of constantan alloy to measure the temperature change of sample and reference material.

Only one pair of thermocouples are used to measure the temperature of the sample and the reference material. In this case, the temperature measured by the thermocouple is substituted into the
heat flow equation to obtain the heat flow at the sample end as follows:

\[ Q_s = \frac{T_s - T_{fs}}{R_s} \]

(1)

The heat flow at the reference end is:

\[ Q_r = \frac{T_r - T_{fr}}{R_r} \]

(2)

Where: \( T_s \) is the temperature of the sample; \( T_r \) is the temperature of the reference; \( T_{fs} \) is the temperature of sample end sensor; \( T_{fr} \) is the temperature of the reference end sensor; \( R_s \) is the thermal resistance of the sensor at the end of the sample; \( R_r \) is the thermal resistance of the sensor at the end of the reference.

The heat flow difference between the sample end and the reference end is:

\[ \Delta Q = Q_s - Q_r = \frac{T_s - T_r}{R} = -\frac{\Delta T}{R} \]

(3)

Where, \( \Delta Q \) is the thermal flow difference, \( \Delta T \) is the temperature difference between the sample and the reference, and \( R \) is the thermal resistance of the sensor.

The above formula is obtained on the premise that the sensor is absolutely symmetrical (that is: \( T_{fs} = T_{fr} \), \( R_s = R_r = R \)), the heat capacity of the sample end and the reference end is equal, and the heating rate of both ends is always equal. In fact, when the calorimeter is working, the temperature distribution on the temperature difference sensor is not uniform, which leads to a large error of the calorimeter.

In order to improve the sensitivity of the calorimeter and reduce the measurement error caused by the uneven temperature distribution on the sensor, the temperature difference sensor of the calorimeter was improved and designed. The structure of the designed high-sensitivity temperature difference sensor is shown in figure 3, which mainly includes: substrate, sample position thermocouple group, reference position thermocouple group. There are many pairs of thermocouples in the sample position thermocouple group and the reference position thermocouple group, these thermocouples are connected in series and distributed uniformly in the whole circumference. Temperature measuring points are set at the connection of each thermocouple, the inner ring temperature measuring point is used to measure the temperature of the sample or reference material, and the outer ring temperature measuring point is used to measure the temperature of the sensor.

![Figure 3. Schematic diagram of high-sensitivity temperature difference sensor.](image)

At this time, the heat flow difference measured by the sensor is:

\[ \Delta Q = \frac{\sum_{i=1}^{n} (\Delta T_i)}{R} - \sum_{i=1}^{n} (\Delta T_r_i) \]

(4)

Where: \( \Delta T_s \) is the temperature difference between the sample and the sensor; \( \Delta T_r \) is the temperature difference between the reference and the sensor; \( R \) is the thermal resistance of the sensor; \( n \) is the number of thermocouple pairs.

At this time, because the thermocouples are evenly distributed throughout the circumference and multiple temperature measuring points are set, even if the temperature distribution on the sensor isn’t uniform, the effect on the measurement result is extremely small. The temperature difference sensor with many pairs of thermocouples has a large amount of original signal acquisition and a good resolution, which greatly improves the sensitivity of the DSC.

4. Finite element analysis of temperature difference sensor

When the temperature difference sensor is working, the uniformity of the temperature distribution directly affects the measurement accuracy of the DSC. In order to obtain the temperature distribution
of the high-sensitivity temperature difference sensor and the dumbbell-type temperature difference sensor under different working temperatures of the calorimeter. Firstly, the finite element models of the two kinds of sensors are established, and then the steady state thermal analysis of the two sensors is carried out under different temperature conditions by using the finite element analysis software ANSYS.

4.1. Establishment of finite element model

The substrate of the high sensitive temperature difference sensor is a disc with a diameter of 30mm and a height of 2mm, on which a circular groove with a diameter of 10mm and a depth of 0.5mm is opened to hold the sample and reference crucible. First of all, the structure of the high-sensitivity and dumbbell-type temperature difference sensors is moderately simplified, and then the 3D models of them are established by using ANSYS modeling tools. Finally, the 3D model is meshes divided, and the area where samples and reference crucible are placed is meshes encrypted to ensure the accuracy and accuracy of thermal analysis. The finite element model of the temperature difference sensor is shown in figure 4.

![Finite element model of temperature difference sensor](image)

Figure 4. Finite element model of temperature difference sensor.

4.2. Finite element analysis of temperature difference sensor

Firstly, setting the material of high-sensitivity temperature difference sensor is alumina ceramic, and the material of dumbbell-type temperature difference sensor is constantan alloy. Secondly, the heat transfer mode and boundary conditions are set respectively, assuming that the sample reaction is exothermic. The working temperature of heat flow DSC is generally as follows: room temperature~200°C, so the finite element analysis of the two sensors was carried out at 25°C, 200°C and 500°C respectively. The finite element analysis results of the high-sensitive temperature difference sensor are shown in figure 5, and those of the dumbbell-type temperature difference sensor are shown in figure 6.

![Temperature distribution of high-sensitive temperature difference sensor](image)

Figure 5. Temperature distribution of high-sensitive temperature difference sensor.

![Temperature distribution of dumbbell-type temperature difference sensor](image)

Figure 6. Temperature distribution of dumbbell-type temperature difference sensor.
According to the results of finite element analysis, when the calorimeter is working, there is a serious temperature gradient on the temperature difference sensor, the temperature difference between the sample end and the reference end of the sensor is large, and even in a single sample end or reference end, there is a certain gradient in the temperature distribution. Under different working temperatures, the difference between the maximum temperature and the minimum temperature on the sensor is shown in table 1.

| Working temperature of calorimeter(℃) | Temperature difference of high-sensitivity temperature difference sensor(℃) | Temperature difference of dumbbell-type temperature difference sensor(℃) |
|--------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 25                                   | 0.303                                           | 0.512                                           |
| 200                                  | 0.3                                             | 0.51                                            |
| 500                                  | 0.31                                            | 0.65                                            |

From the data in table 1, it can be seen that the temperature difference of the high-sensitive temperature difference sensor under different working temperatures is smaller than that of the dumbbell-type temperature difference sensor, and the reduction range is 40.8% ~ 52.3%.

5. Conclusion
The performance of the DSC is improved by improving the design of the temperature difference sensor.

(1) From the theoretical analysis and calculation, it can be seen that the use of multiple pairs of thermocouples connected in reverse to form a radial thermocouple group can reduce the measurement error caused by the uneven temperature distribution of the sensor, and the original signal collection of the sensor is large.

(2) It can be seen from the results of finite element analysis that the temperature difference of the high-sensitivity temperature difference sensor is 40.8% ~ 52.3% lower than that of the dumbbell-type temperature difference sensor under different working temperatures. The temperature uniformity has been improved, so the error caused by the uneven temperature distribution has been further reduced, and the accuracy of the calorimeter has been greatly improved.

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