DIFFERENTIAL SCANNING CALORIMETER

The present application claims priority based upon U.S. Provisional patent application Ser. No. 60/032,051, filed Nov. 1, 1996.

BACKGROUND

1. Field of the Invention

The present invention relates to heat flux different scanning calorimeters, and to the temperature sensors used in such calorimeters.

2. Background of the Invention

Heat flux differential scanning calorimeters (DSCs) are described in U.S. Pat. No. 5,224,775, which is incorporated herein by reference. Heat flux DSCs measure temperature differences within the DSC, which are proportional to the flow of heat to the sample. The temperature differences are measured using sensors at the sample position and at the reference position. The temperature differences are calibrated, such that the heat flow to the sample can be measured, as the sample and reference materials are subjected to dynamically controlled changes of temperature. Plots of the sample heat flow as a function of temperature provides information concerning physical transformations occurring in the sample material.

The sensor assembly in heat flux DSCs include temperature sensors mounted on a support structure which is mounted in an oven, which is a source or a sink for heat flowing into (or out of) the sensor assembly. The sample temperature sensor and the reference temperature sensor are attached to the sample and reference positions of the support structure. The sample temperature sensor measures a temperature representative of the temperature of the sample, and the temperature difference signal is obtained by measuring the difference between the sample and reference temperature signals. The sample temperature sensor is calibrated so that it closely matches the actual sample temperature, and the differential temperature sensor is calibrated to provide an accurate measure of the heat flow to (and from) the sample.

The measured temperature difference is created by the flow of heat between the oven and the sample and reference via the support structure. Thus, the measured temperature difference between the sample position and the reference position is dependent upon the geometry of the supporting structure, and on the thermal diffusivity of the material from which the supporting structure is constructed.

In principle, any of type of temperature sensor or differential temperature sensor may be used in a DSC. The most common types of temperature sensors used in heat flux DSCs are thermocouples, thermopiles and resistance temperature detectors (RTDs). Thermocouples and thermopiles generate a voltage which depends upon the temperature of the junction. Using calibration tables, the temperature of the junction between thermoelectrically different materials can be determined from a measurement of the voltage. However, the voltage generally becomes progressively smaller as temperature decreases, which reduces the sensitivity of thermocouple temperature sensors at lower temperatures.

Because the electrical resistance of a conductor depends on the temperature of the conductor, RTDs measure temperature by measuring the resistance of a conductor, and using appropriate calibration procedures and tables to compute the temperature of the conductor from its resistance. The most widely used type of RTDs are platinum RTDs. For platinum RTDs, the resistance of the platinum decreases with decreasing temperature. If a known electrical current is passed through the platinum RTD, the resultant voltage which appears across the terminals of the RTD is a measure of the temperature of the RTD. The output voltage of the RTD is directly proportional to the applied current, so increasing the current increases the RTD signal, making high currents desirable.

Because of the variation of the voltage output of the temperature sensor as a function of temperature, and the variation of thermal diffusivity of the supporting structure as a function of temperature, the voltage output of a conventional DSC sensor varies considerably with temperature. Typically, the voltage output of a differential thermal analysis sensor falls rapidly below ambient temperature. Furthermore, because transitions which occur at low temperatures are generally quite weak, detection of low temperature transitions is particularly difficult as temperatures decrease.

The dynamic response of a sensor for a DSC is a parameter that describes how rapidly the sensor reacts to a change in heat flow. Sensors with rapid dynamic responses are desirable for three reasons. First, if the sensor has a slow response, the measured temperature will lag the actual temperature. Second, if two transitions occur at temperatures which are in close proximity to each other, the overlap of the two transitions will be greater if the sensor has slow response. Third, in the Modulated DSC® technique (MDSC®), which is described in U.S. Pat. No. 5,224,775, the sample temperature is driven by the combination of a linear temperature ramp and a superimposed periodic temperature variation. When sensors with slow dynamic responses are used to perform MDSC measurements, the choices of the ramp rate and the period of the temperature modulation can be limited by the slow dynamic response of the sensor.

In conventional DSCs, calorimetric sensitivity and dynamic response have an inverse dependence: increasing the calorimetric sensitivity decreases the dynamic response, and vice versa. This is because rapid dynamic response is obtained by increasing the rate at which heat can be transferred between the oven and the sample and reference. The rate of heat transfer between the oven and the sample and reference is dependent upon the thermal resistance of the support structure: decreasing thermal resistance of the support structure increases the rate of heat transfer to and from signal and reference, and decreases the measured temperature difference between sample and reference and hence the measured signal for a given heat flow.

The flow of an electric current through a conductor generates heat equal to the product of the resistance of the conductor and the square of the current. Heat generated within the resistance element of an RTD by this mechanism causes temperature measurement errors because the heat generated increases the temperature of the element resulting in a high temperature measurement. This is known as "self-heating error". The magnitude of the resultant error depends upon how much heat is generated and how well the heat can be dissipated, which in turn depends upon how the RTD is constructed and mounted. Because of the uncertainty introduced by these factors, the conventional approach has been to keep RTD currents as low as possible while maintaining a sufficiently high RTD output.

RTD sensors generally fall into two categories, wire-wound RTDs and thin film RTDs. Wire-wound RTDs use a fine platinum wire wound on an electrically insulating support as the resistor. The resistor is inserted in an electri-