

ance between sample and reference sides of the structure. To correct the imbalance, the quotient of the output voltage and the RTD resistance is taken, which gives a current. The resulting current, which could be called the unbalance current, is applied to the 1 ma excitation currents by subtracting half of the unbalance current from the 1 ma current for the sample side and adding half of the unbalance current to the 1 ma current for the reference side (note that the sign of the unbalance is included in the calculation). The resultant currents are stored, and are the currents which will correct the DSC zero heat flow line.

#### Excitation Current Determination

The variable excitation current which will give constant calorimetric sensitivity (volts/watt) is determined by running a 25 mg sapphire sample using the base excitation currents determined in the previous step. The sapphire sample is carefully weighed and loaded in a sample pan. A reference pan is selected that matches the sample pan very closely. A scan is run over the temperature range of interest, and the heat flow voltage signal, sample temperature and heating rate (i.e., the derivative of sample temperature with respect to time) are recorded and stored. The expected heat flow to the sapphire sample is computed as a function of sample temperature, from the sample temperature and the heating rate, using the known heat capacity of sapphire as a function of temperature. The quotient of the output voltage and the computed sample heat flow is calculated. This is the calorimeter heat flow signal, with zero heat flow correction. The calorimeter heat flow signal is then divided by the desired sensitivity, in volts/watt, to give a dimensionless number, which is multiplied by the zero-corrected excitation currents for both the sample and the reference to provide the excitation currents for constant calorimetric sensitivity.

The choice of desired sensitivity is not an arbitrary choice, because increasing the sensitivity will usually result in increased noise levels. Thus, the choice of sensitivity depends upon the level of noise that can be tolerated. Of course, high noise levels ultimately limit the instrument sensitivity, because then weak thermal events cannot be distinguished from the noise. These currents are implemented by the sample current function **39** and the reference current function **36**.

#### Sample Heat Flow Calibration

Heat flow calibration is performed using a sample with a well characterized physical transformation, for example, the melt of a metal such as indium, which occurs in the temperature region of interest for subsequent experiments. A sample is carefully weighed and loaded into a pan and installed in the calorimeter, a closely matched empty pan is installed on the reference position of the calorimeter. A heating scan is run at heating rate equal to the rate that will be used in subsequent experiments. The enthalpy of the transition is measured by integration of the peak area and compared to known values. The ratio of the measured to the standard value is used as a multiplier to scale the output of subsequent experiments.

Calibration of the sample temperature is carried out in the normal fashion, using a series of standards which have well-characterized transitions to correct the sample temperature using a curve fitted to the differences between the measured and correct temperatures for the transitions.

A second embodiment of the present invention, using an alternate metallic disk differential scanning calorimeter is shown schematically in FIG. 3. FIG. 3 is a bottom view of

the sensor assembly, looking upward at the underside of the metallic disk. The sample and reference pans are placed upon the opposite (top) side of the disk.

Sample RTD **62** is held tightly against metallic disk **61** by clip **64**, which is attached to disk **61** in a conventional manner using, e.g., welding. Similarly, reference RTD **63** is held tightly against metallic disk **61** by clip **65** which is similarly attached to disk **61**. The RTDs are commercially available thin-film RTDs which have been deposited on an  $Al_2O_3$  substrate, e.g., Hy-Cal Model EL-700, available from Hy-Cal Sensing Products, El Monte, Calif. The sample RTD and the reference RTD are in intimate contact with the disk, and are located directly beneath the sample and reference positions. The RTDs thus measure the temperature of the sample and reference regions of the sensor, which are a measure of the sample and reference temperatures, respectively.

The sensor assembly is mounted to the DSC oven at the periphery **70** of metallic disk **61**. Lead wires **66** and **68**, of the sample and reference RTDs, respectively, each have a pair of extension wires (not shown in FIG. 3) attached. For each RTD, one of the extension wires is used as the current source lead, and the other extension wire is used as the voltage sensing lead. The remaining lead wires, lead wire **67** on the sample RTD and lead wire **69** on the reference RTD also each have a pair of extension wires (not shown) attached. One of the extension wires for each of the RTDs is used connected to ground, and the other is used to measure the voltage appearing across the RTD. The extension wires are connected to the DSC system shown in FIG. 2, similarly to the lead wires of the sensor assembly shown in FIG. 1.

Although the thin film RTD element is not deposited directly on the disk as in the first embodiment, temperature measurement errors due to Joule heating of the RTD are relatively small because the disk to which the RTDs are attached is a relatively good heat conductor. For example, Hy-Cal Model EL-700 thin film RTD, shown on page A10 of the Hy-Cal Summer 1996 catalog, may be used. With a sensing current of 2.3 ma, the temperature rise of the RTD (with respect to the surface temperature) is just  $0.02^\circ C$ . This temperature rise only results in very small errors, which are further minimized when using the temperature calibration procedures described above. Also, the excitation current of 2.3 ma is more than twice as large as the maximum excitation current of 1 ma recommended for this sensor in general purpose applications. The disk in this sensor assembly is metallic, and is a good thermal conductor, as described above.

Another preferred embodiment of a DSC sensor for use in a constant sensitivity DSC is depicted in FIG. 4. The support structure **81** consists of a pair of lugs **82** and **83** and a base **84**. The lugs are symmetric with respect to the base structure and form the supports for the sample and the reference. Lug **82** is the sample lug and has a thin film RTD **85** deposited on the same side of the lug as the base. The sample pan (not shown) is placed on the opposite side of the lug from the RTD directly opposite to the RTD. Lug **83** is the reference lug and has a thin film RTD **86** deposited on the same side of the lug as the base. The reference pan (not shown) is placed on the opposite side of the lug from the RTD directly opposite to the RTD.

A pair of lead wires is attached to each end of both RTDs. Lead wire **87** of the sample RTD supplies excitation current to the sample RTD, and lead wire **88** is attached to the ground. Lead wires **89** and **90** are the voltage sensing leads, the voltage representing the RTD resistance (and hence its