Differential Thermal Analysis Calorimeter at the Naval Research Laboratory

D.L. Knies, K.S. Grabowski, D.A. Kidwell and V.K. Nguyen
Materials Science and Technology Division, Naval Research Laboratory, Washington, DC 20375

M.E. Melich,
Wayne E. Meyer Institute of Systems Engineering, Naval Postgraduate School, Monterey, CA 93943

Abstract Differential thermal analysis (DTA) is a standard thermoanalytic technique used widely in industry and research. Drawing on this concept, DTA based calorimeters are under development at the Naval Research Laboratory (NRL) for the study of hydrogen in metals. The design goals are: high sensitivity, linear response, short time constant, tolerant to ambient temperature variations, easy to adapt to experimental constraints and low cost. In this paper we detail basic design requirements, and show a number of examples of their implementation.

1. Introduction

Since the announcement of thermal anomalies in the palladium-deuterium system reported by Fleischmann & Pons [1] in 1989, now referred by many as the Fleischmann Pons Effect (FPE), the veracity of their results have been questioned by the wider scientific community. Much of this criticism has been leveled at the calorimetry and its interpretation. Since then, the complexity of calorimeters used to confirm or refute the original isoperibolic calorimeter results has added to the confusion. One example of calorimeters applied is a first principles mass flow calorimeter, as was reviewed by McKubre et al. [2]. These are complicated systems requiring a large capital investment, and are not well suited for broad materials studies. To circumvent these limitations, we investigated commercially available calorimeters and analyzed their operating principles. None was found that met all our needs to study materials related to FPE. However, the basic operating principle for the differential thermal analysis (DTA) class of calorimeters held the promise of meeting this need. This paper describes the operating principle of DTA and our prototype implementations of DTA concepts specifically geared for the study of FPE-related materials.

2. Approach

The rejection of common mode signals is an integral part of the design of a DTA calorimeter. The technique relies on using two nearly identical thermal masses connected to a thermal reference (Fig. 1). The ability to reject common mode signals is dependent on the careful physical layout and shielding of the measurement channels. In our case, one of the thermal masses is an inert cell, while the other is the active cell. The analog electric circuit equivalent is a common mode amplifier, in this case, used to remove stray thermal signals generated by fluctuations in the ambient or reference temperature. In the ideal case

$$V_{out} = A^*(V_{inert} - V_{active})$$

where A is the difference gain, and V is the voltage generated by thermoelectric modules. Thermoelectric modules (TEM) monitor the flow of heat from the inert and active cells to the common thermal reference. The cell output voltages are given by

$$V = \alpha N(T_{cell} - T_{ref})/(1+2r l_c/l)$$

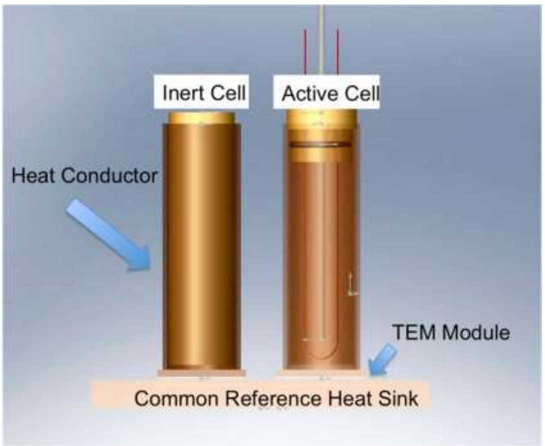

Figure 1. Conceptual drawing of a DTA calorimeter.

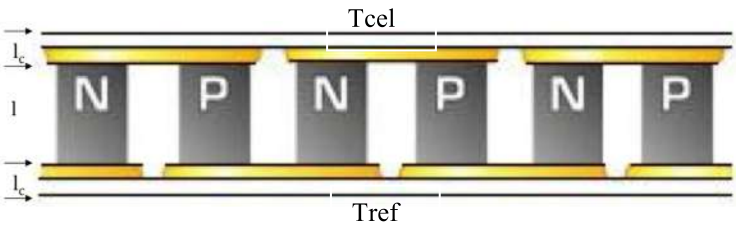

Figure 2. Graphical representation of thermoelectric module.

according to Rowe et.al. [3], where α is the Seebeck coefficient of the thermoelectric material, N the number of thermocouples, *l* is length of the thermoelement, l_c, the thickness of the contact layer, T_{cell}, and T_{ref}, are temperatures at the cell and reference sides of the module and $r = \lambda/\lambda_c$, where λ the thermal conductivity of the thermoelement and λ_c the contact thermal conductivity as shown in Fig. 2.

Rather than paneling the inside of a box with many TEMs as was done by Stroms [4], only two TEMs were used - one for the active cell and one for the inert cell (Fig 1). Heat flow was directed to the TEM by surrounding the active cell volume by a good heat conductor. A finite element analysis calculation was done to understand the steady state heat flow pathway for this approach. The result of this study can be seen in Fig. 3. The largest temperature gradient is across the TEM , thus, that is where the bulk of the heat flows. The time constant of the cell can be adjusted by the thermal mass and thermal properties of the cell. The cells should be surrounded by a constant temperature bath of very low thermal mass. This can be accomplished by surrounding the cell with a large thermal mass at the reference temperature, and leaving a small air gap between it and the cell. These basic principles have been used to tailor calorimetric systems to specific tasks since the invention of the thermocouple.

3. Experimental

The basic DTA concept can have nearly unlimited variations and can be tailored to satisfy specific applications. We tested two basic test tube designs. The first DTA is built around a disposable BD Falcon™ 50 ml conical tube. It can house either a simple cathode and anode assembly for electrolytic loading or a gas bottle for gas phase experiments. The heat transfer tubes were machined from two pieces of aluminum such that the 50 ml test tubes fit tightly. A large scrap piece of aluminum (26 cm x 21.6 cm * 3.81 cm) was used as the reference heat sink. The bottoms of the heat transfer tubes and the top of the reference heat sink were polished where the TEM’s where to be attached. Two Custom ThermoElectric 40 mm x 40 mm TEM modules (part# 12711-5L31-03CQ) were silver printed to both the heat transfer tubes and the reference heat sink. The heat transfer tubes were then insulated using Armacel AP/Armaflex Microban 25/50 pipe insulation. Identically insulated hand wound 23 ohm nichrome wire heaters were

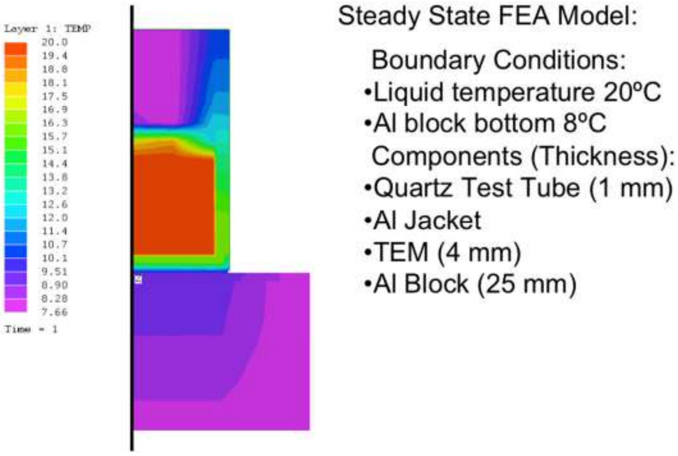

Figure 3. - Steady state FEA model of active cylindrical cell. One-half of symmetric cell is shown in cross section.

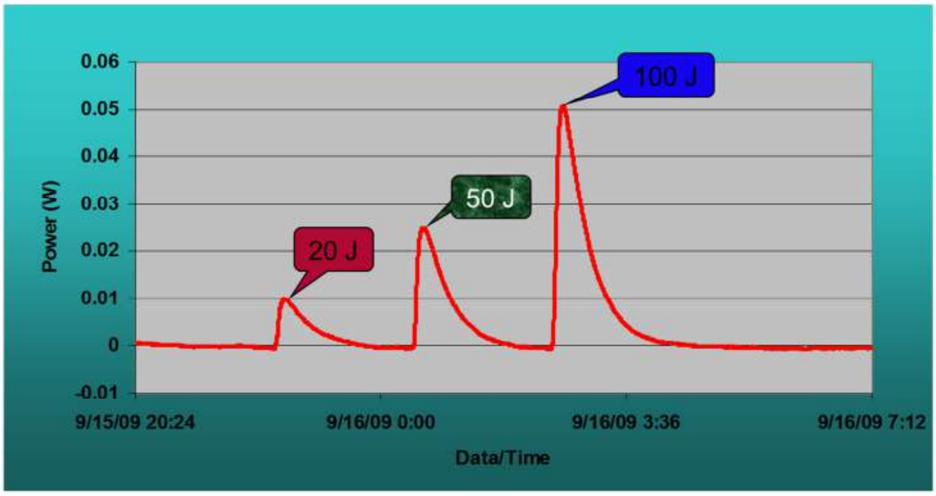

Figure 4. - DTA baseline stability and pulse response.

Table 1. - DTA response to a gas loading simulation

Impulse	**Measured**	**Error**
20 J	19.8 J	1% / 0.2 J
50 J	46.1 J	8% / 3.9 J
100 J	94.6 J	5% / 5.4 J

installed in both the reference and active cells. RTDs for temperature measurement were installed along the centerline of the cells. The completed system was then placed inside an incubator.

The DTA was tested for baseline stability and pulsed heat response to simulate our typical gas loading experiment [5]. The performance was evaluated by programming a Bio-Logic USA, LLC Model VSP potentiostat / galvanostat in constant power mode to produce 20, 50, and 100 joule pulses. Shown in figure 4 and table 1 are the results of this test. The agreement between the measured response and the delivered power is comparable to commercially produced instrumentation.

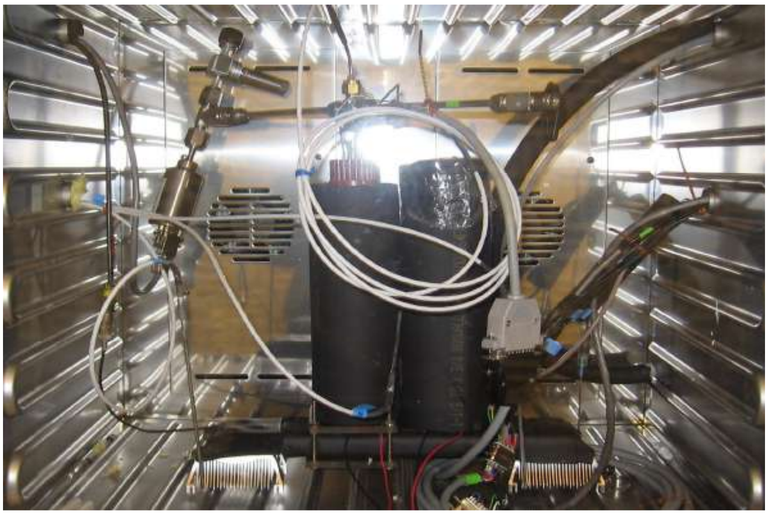

Figure 5. - Fully assembled DTA Calorimeter.

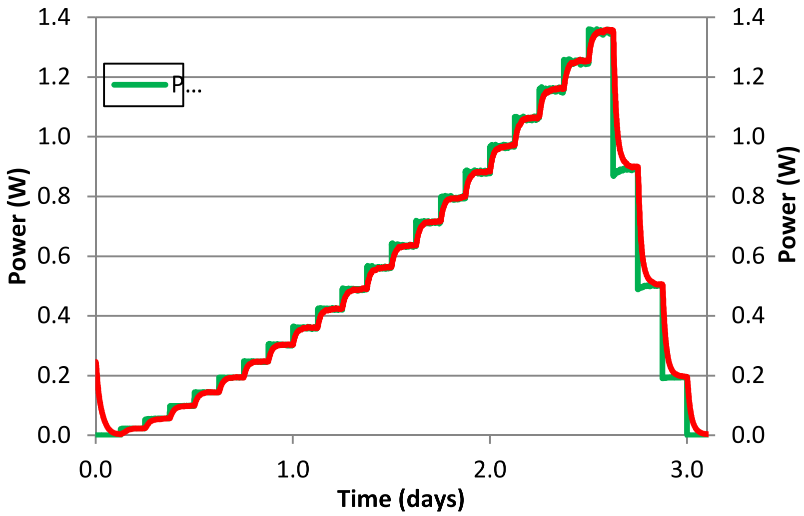

Figure 6. - Calibration run of DTA designed to match ENEA cell.

The second proof of principle DTA system was built to match the ENEA Violante closed cell design [6].The design concept is basically the same as the first. The heat transfer tubes are built from commercially available copper pipe machined to match the outside dimension of the ENEA electrolytic cell. The fully assembled DTA is shown if Fig. 5. Results of a 3 day calibration run using light water are shown in Figure 6, where the current was stepped under galvanostatic control over a typical operating range. A single linear combination of the inert and active cell TEM voltages fit the input power of the tested range. The maximum power is limited by the heat sink's capability to transfer heat to the incubator. The inside temperature of the cell was monitored by RTDs, and also correlates with the input power as expected. Two heat sinks on either end of the thermal reference were also monitored. Their temperatures were also well correlated with the input power.

4. Conclusions

These proof of principle tests clearly demonstrate that one can build a very capable calorimeter that satisfy the needs of a rapid materials development and screening program, to gain insight underlying the requirements for the FPE. These simple systems proved to be stable (1% over 5 days) with good sensitivity (1% absolute) comparable in many ways to our commercial Hart Heat Conduction calorimeter. The concepts can readily be modified to include, for example, external stimuli of time varying magnetic or electric fields, laser stimulation and programmable temperature ramps. This makes this design an ideal platform to test the validity of FPE claims in both liquid and gas phases. The linear response obtained over the tested operating range from a few Joules of impulse heat to long-term hours of operation at several watts DC makes the interpretation of results straightforward.

References

[1] M. Fleischmann, S. Pons and M. Hawkins, J. Electroanal. Chem. **261** (1989) 301; *Errata* 263 (1989) 187.

[2] McKubre, M.C.H. and F. Tanzella, Mass Flow Calorimetry, in ICCF-14 International Conference on Condensed Matter Nuclear Science. 2008. Washington, DC.

[3] D.M. Rowe, G.Min, IEE Proc.-Sci. Meas. Technol. **143** (1996) 351.

[4] Storms, E., 12^{th} International Conference on Condensed Matter Nuclear Science. 2005. Yokohama, Japan.

[5] D.A. Kidwell, A.E. Rogers, K.S. Grabowski, D.L. Knies, 15^{th} International Conference on Cold Fusion, Rome, Italy, October 5-9, 2009

[6] Violante, V., Sarto, F., Castagna, E., McKubre, M. C. H., Tanzella, F. L., Hubler, G. K., Knies, D., Dardik, I., Sibilia, Joint Scientific Advances in Condensed Matter Nuclear Science. in 8th International Workshop on Anomalies in Hydrogen / Deuterium Loaded Metals. 2007. Sicily, Italy.