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A DTA instrument based on optical measurement of temperature ☆

Jai S. Subramanian[a], Patrick K. Gallagher[a,b,*]

Departments of Materials Science [a], and Engineering and Chemistry [b], The Ohio State University, Columbus OH 43210-1173, USA

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Abstract

A DTA instrument has been designed around the Acufiber Model 100C temperature measurement and control system. The temperature of the sample and reference materials are determined by their black body radiation. This radiation is conveyed through single crystal sapphire light-pipes that also act as supports for the sample and reference. The ΔT signal is determined by subtraction and the temperature of the reference material is used to control the furnace temperature. These preliminary investigations on the optical differential thermal analysis (ODTA) have been encouraging and considerations of the effects of emissivity are being explored.

Keywords: DTA; Emissivity; Optical sensors; Thermal analysis instruments

1. Introduction

Differential thermal analysis (DTA) has found considerable use for the detection of phase transitions and solid state reactions at elevated temperatures. At temperatures above about 1600°C, however, the conventional use of thermocouples as temperature sensors becomes very limited and controlled atmospheres are generally required. Their sensitivity drops off and, because of the need for good thermal contact with the sample, the possibilities of reactions with the sample or its holder increase. That same contact with the sample also represents a path of thermal leakage, and hence a perturbation on the measurement.

* Corresponding author.

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If the temperature were measured optically using the laws for black body radiation, many of these limitations would be alleviated. Perhaps even more importantly, it would become possible to monitor thermal events in supported thin films with much greater sensitivity by virtue of the elimination of the thermocouple contact and thermal leakage.

The availability of high quality optical systems for the measurement and control of temperature encourages studies on the feasibility of an optical DTA [1]. The following sections describe such a preliminary study and present encouraging initial results which do indeed clearly demonstrate the practicality of such instruments.

2. Experimental

The optical thermometer marketed by the Luxtron Corporation was selected as the starting point. The Accufiber Model 100C has a dual sensor configuration that is ideal for this purpose. An example (Accufiber applications note [2]) of the relative noise observed in such a system compared with that for a comparable noble metal thermocouple device is shown in Fig 1. The peak-to-peak noise observed is about 0.5°C for the thermocouple, but less than 0.01°C for the optical sensor. This suggests that the ultimate sensitivity obtainable from such an optical DTA will be determined by the ability to program and control the temperature of the furnace precisely.

Two single crystal light-guides are provided with suitable polished surfaces. These were also used as the support system for the sample and reference crucibles as shown in Fig. 2. The proximity of the light-guide to the sample is highly flexible based upon the optical systems used to focus the emission onto the opening of the light-guide. For this initial venture the sample and reference crucibles were supported about 1 mm above the ends of the guides. The cool ends of these light-pipes are coupled to optical fibers that conduct the signal to the measurement and control unit. Several crucibles were tried and alumina crucibles used in conventional DTA were found suitable. The

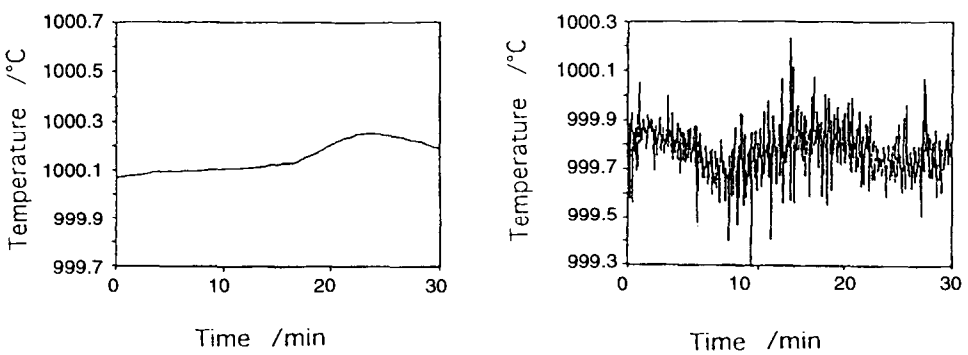

Fig. 1. Noise comparison between optical fiber thermometer (left) and a noble metal thermocouple (right) at 25 Hz.

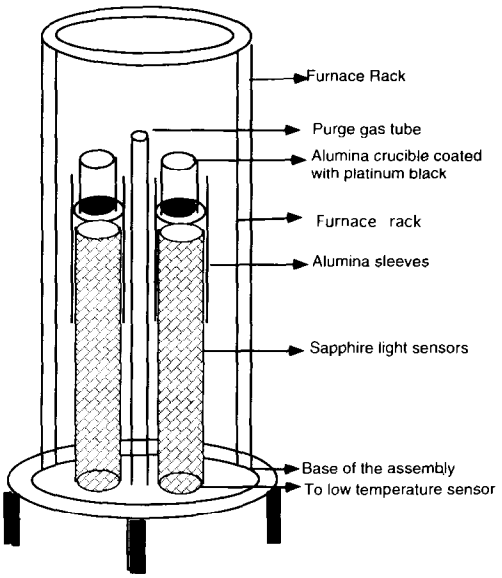

Fig. 2. The optical DTA assembly with the accompanying furnace.

undersides were coated with platinum black to provide a relatively good and reproducible black body emitter.

The control module coupled with the manufacturer's software converts the optical signals, derived from the radiant emission by the sample and reference, directly to temperature in accordance with Planck's law, where E_b represents the energy emitted at the wavelength, λ, and temperature, T. C_1 and C_2 are constants. See Ref. [1] for further details.

$$E_b(\lambda, T) = C_1 \lambda^{-5} - \exp(-C_2/\lambda T). \quad (1)$$

The value of ΔT is simply obtained by subtracting the temperature of the reference from that of the sample. The temperature of the reference is also used to control the furnace temperature in accordance with the PID hardware and software supplied by the manufacturer.

Although the sensor is capable of measuring temperatures above 2000°C, the alumina crucibles and supported rods limited the upper temperature of this initial system. Consequently a furnace capable of 1700°C was selected. The furnace and its support system are essentially those of the Harrop high temperature DTA. The entire system is capable of operating in both oxidizing and reducing atmospheres at the rated temperature.

3. Results and discussion

The system was calibrated using the melting point of gold. An emissivity value of 0.87 was used for an atmosphere of flowing argon (50 ml min^{-1}) and a heating rate of 20°C

min^{-1}. This gave a value for the melting point of 1064°C. The onset temperature was unchanged at a heating rate of 10°C min^{-1} as seen in Fig. 3. The reduced dependence of the transition temperature on the heating rate can be attributed to the improved thermal isolation of the sample and reference in an optically based system. All subsequent measurements were performed in an argon atmosphere, at a heating rate of 20°C min^{-1} and an emissivity value of 0.87 was used to calculate the temperature of the sample.

The noise levels in the actual measurement were higher than the levels indicated by the manufacturer. Some possible explanations include: PID parameters not being optimized, nonbifilar windings of the furnace elements, and the larger size of the furnace compared to the commercial DTAs.

As examples of first order phase transformations within the temperature range of this instrument, the melting of cobalt and the hexagonal-to-rhombohedral transition of strontium carbonate were selected. The melting of cobalt had an onset temperature of about 1496°C as can be seen in Fig. 4. The phase transition for a sample of strontium carbonate during its second heating in carbon dioxide is shown in Fig. 5. The onset temperature for the reheat was at 934°C, consistent with other work in carbon dioxide [3,4].

The ability to detect weak second order transformations was tested using the Curie temperature (ferromagnetic-to-paramagnetic transformation) for cobalt and the ferroelectric-to-paraelectric transformation in lithium niobate having the congruent melting composition [5]. These transitions do not have a change in enthalpy but only a change in the heat capacity. The resulting optical DTA curves are presented in Fig. 6. These very weak transitions can be detected satisfactorily.

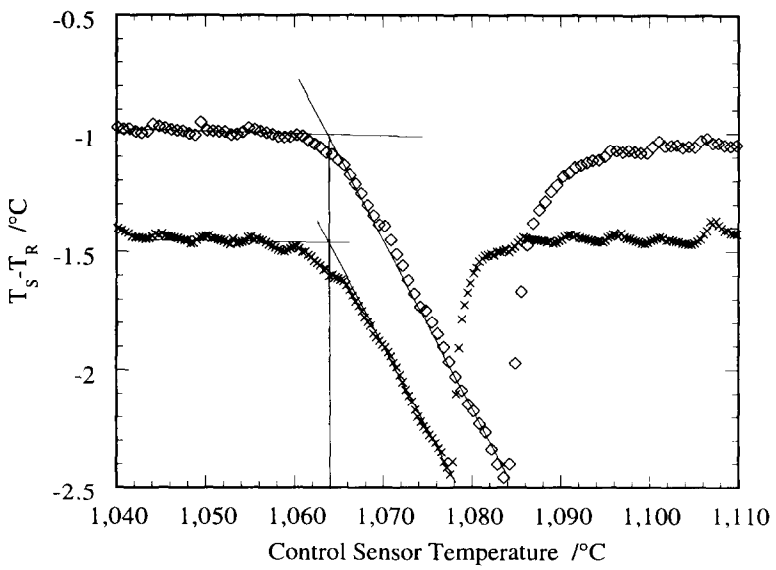

Fig. 3. Melting of 29.61 mg of gold at (×) 10°C min^{-1} and (◇) 20°C min^{-1} in the ODTA.

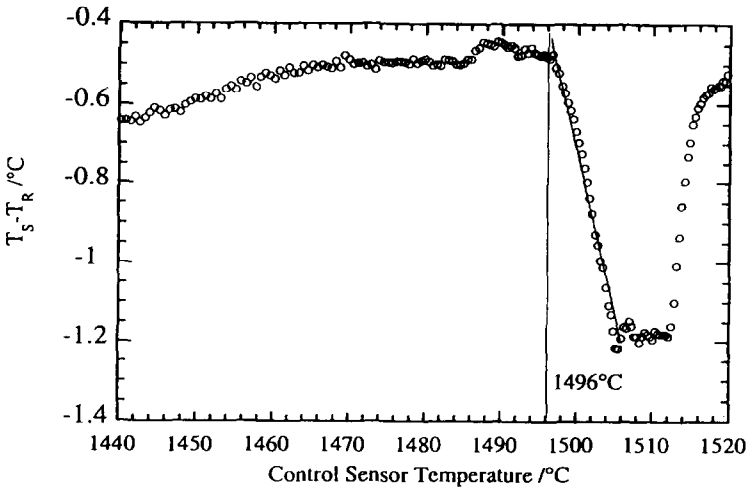

Fig. 4. Melting of 27 mg of cobalt in the ODTA.

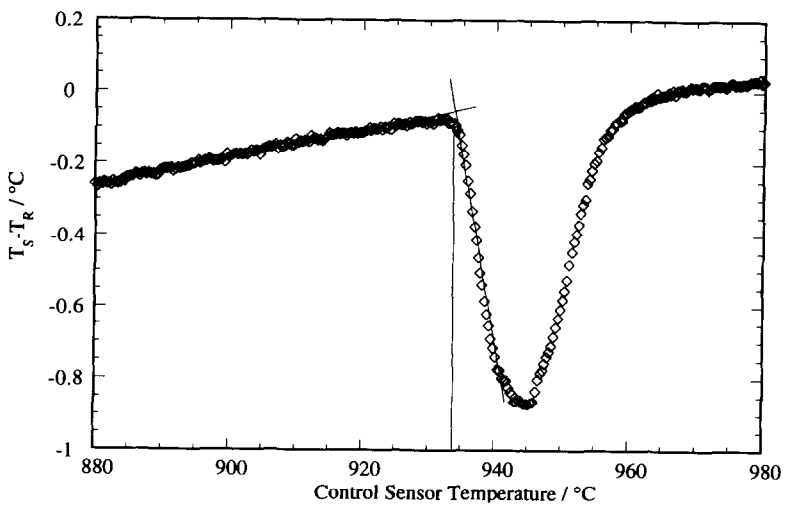

Fig. 5. The hexagonal-to-rhombohedral transition in 40.35 mg of strontium carbonate in the ODTA.

4. Conclusions

These initial results clearly demonstrate not only the feasibility of ODTA but also indicate the high sensitivity and excellent accuracy that can be obtained from a properly calibrated instrument. Work is underway to further demonstrate the usefulness of this approach to study transformations and reactions in thin films. The ability to sense

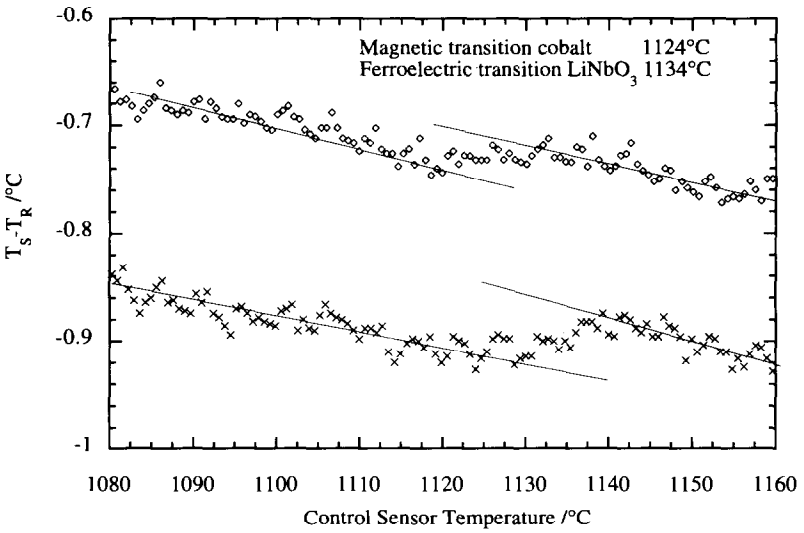

Fig. 6. Second order transitions in (◇) cobalt and (×) lithium niobate in the ODTA.

the temperature of the surface rather than the bulk should markedly improve the usefulness of DTA to study supported thin films.

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