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APPLICATION OF NEW INSTRUMENTATION AND MEASUREMENT TECHNIQUES TO THERMAL ANALYSIS OF MATERIALS

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Principles and operation of the infrared gold image furnace are discussed and its advantages over conventional resistance furnaces for studies of advanced materials listed. Using the gold image furnace in combination with a standard microscope allows continuous monitoring of materials to very high temperatures. New approaches to measurement of heat capacity and thermal diffusivity/conductivity are also described.

Keyword: infrared gold image furnace, semiconductors, superconductors

Introduction

The explosion in materials development has produced substantial quantities of new and improved, but often expensive, products. In many cases the materials have to be produced in special forms and combinations having optimum properties based on specific purities, inhomogenities, heat treatments etc., each requiring that fabrication and characterization be undertaken under especially clean environments and at faster heating and cooling rates than those used in more conventional thermoanalysis.

This has stimulated the development of new thermal technology instrumentation for fabrication and qualitative analysis of materials together with new and modified techniques for determining quantitative thermal properties and performance. In the latter case this has required that measurement be made more rapidly often on special forms and under conditions that cannot be satisfied using appropriate classical methods.

Historically, thermoanalysis and thermal parameter determination were considered distinct and separate tools in development and characterization of materials. The former has been considered primarily as the means to obtain essential qualitative information on structure and behaviour during development, and the latter provides necessary quantitative performance values for a material and/or its applications. Classical thermal analysis techniques used 'small' test specimens and were undertaken rapidly under transient conditions, whereas quantitative methods, generally required 'large' specimens and were time consuming.

More recently the critical issue became the numbers and types of materials requiring investigation. Results were required on smaller specimens and with high precision. This was the major stimulus for development of new or modified methods based on transient techniques for transport properties. As a result of these stimuli it has been found that some of these newer quantitative techniques can also be used for qualitative purposes.

The present paper describes two tools developed especially for use in fabrication and analysis of many new materials. In addition, it includes the essential principles of several newer methods and gives examples of their use as thermoanalytical tools.

Techniques, instrumentation and applications

Infrared gold image furnace

Many 'new' materials such as semiconductors, superconductors and composites require fabrication in very clean high-vacuum or gaseous environments. In some cases particular, precisely controlled temperatures and/or heating, cooling or cycling rates are required. In addition, various applications such as re-entry from space, and rapid thermal annealing can require that relevant thermal analysis studies be made at heating rates that are well in excess of those attainable with conventional restively-heated furnaces.

These requirements are met by the infrared gold image furnace. This radiation furnace, combined with a specially designed temperature controller, consists essentially of one or more high-power-density tungsten filament argon of halogen sealed quartz tubes together with one or more very high reflective, water-cooled, elliptical, parabolic, or planar gold surface reflectors. These surround an appropriate size quartz tube containing the artifact to be heated in the required contaminant-free environment. The result is a compact, low-mass, energy efficient, maintenance-free system that allows different types, and forms of specimen to be heated and cooled at heating rates from the conventional 1 to 100 deg·min^{-1} up to many hundreds of degrees per minute.

A comparison of the features of the gold image furnace with those of conventional resistance furnaces is shown in Table 1. These individual furnaces and larger systems based on them have found very wide use for many applications.

Table 1 Comparison of comparable gold image and resistance heated furnaces

Characteristics	Infrarad gold image	Resistance
Heat transfer for mechanism	Radiation from quartz lamp	Conduction and convection of local environment. Radiation at high temperatures
Heat capability	High power density Low heat capacity	Low power density Large heat capacity
Heating uniformity	Large zone on heating and cooling	Uniform zone obtained only at a constant temperature
Temperature control	Direct using specimen temperature pre-use control of rate and actual	Control by sensor in proximity to heating element.
Response	Fast	Slow
Heating rates	Up to 100 deg·min^{-1}	Max. 100 deg·s^{-1}
Cleanliness	No source of contamination	Exposed heater and insulation sources of contamination
	Cold wall	Hot wall
Other	Energy efficient, compact, dust-free	Less compact, less efficient, susceptible to dust production.

These include the development and production of materials and components especially semiconductor and coated composites, continuous annealing of steels and other materials and simulation of processes to develop other materials with optimum properties. In addition, they have also been fitted to other test instruments, especially those for TG, DTA and dilatometry.

High-temperature surface observation furnace

A new development incorporating the gold image furnace is using it in combination with a standard microscope, CCD colour camera and monitor to allow continuous visual analysis of materials to very high temperatures. In contrast to a 'hot stage' no special optics or mechanical conversions are required.

Since the lamp acts simultaneously as the heating and light sources the system is compact and can be attached directly and simply such that the specimen remains focused continuously as shown in Fig. 1. These systems are used extensively to study surface-related behaviour including phase transitions, melting and solidification, crystal and oxide growth, sintering and deposition processes, thermal shock, surface adhesion and measurements of contact angle. A further extension of this development is to combine the furnace system microscope with a particular thermal analysis instrument in order to undertake and record simultaneous visual behaviour with change in length, mass or other thermoanalytical parameters.

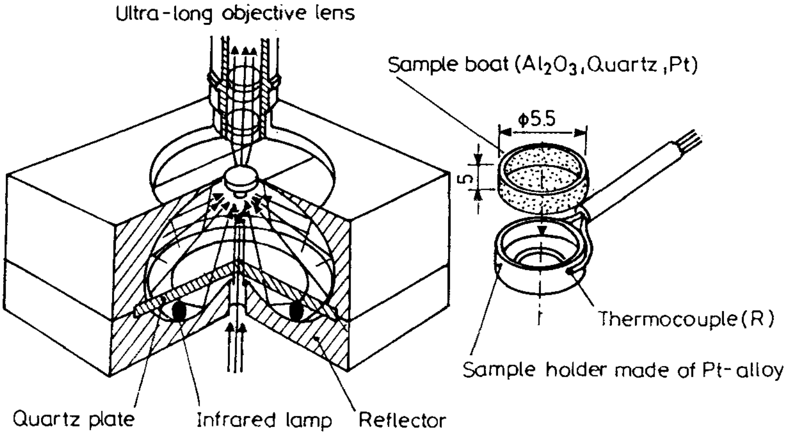

Fig. 1 Sinku-Riko high-temperature furnace microscope system

Measurement of heat capacity

During the past two decades DSC has been the predominant method used, especially for moderate temperatures up to 500°–600°C. The attraction is its use of milligram quantities of materials. While it is used extensively for quantitative measurements it is not a panacea. Drawbacks exist, particularly in its use for heterogeneous media where the small specimen size is not representative of the bulk of material. In addition, results obtained on different forms of the same material are variable, dependent on heating rate and often not sensitive enough to quantify second and third order transitions. These factors also prevent it being suitable for thermal conductivity determination. Other techniques not requiring the large specimen amount needed for adiabatic and drop calorimetry are thus necessary to supplement DSC.

One new method developed as a very sensitive tool, particularly useful for materials in the form of thin films and sheets, is the ac calorimeter [1]. Figure 2 illustrates schematically the principle on which it is based. The front surface of a specimen is irradiated by light from a halogen lamp, chopped at frequency, f (usually between 0.01 and 30 Hz). By using a specially designed very precise lock-in amplifier the small temperature amplitude T_{ac} is measured on the rear surface of the specimen.

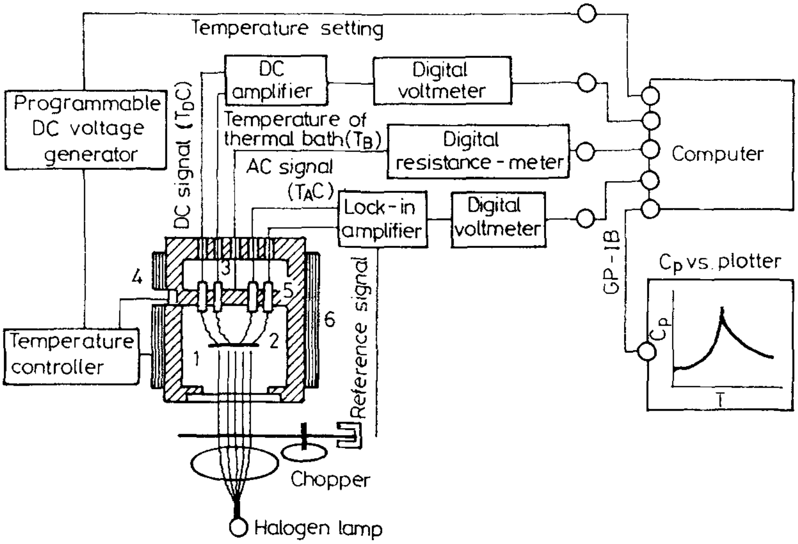

Fig. 2 Schematic of the principle of ac calorimeter. 1 Specimen, 2 Thermocouple, 3 Pt Thermometer for temperature measurement, 4 Pt Thermometer for temperature controll, 5 Thermal bath, 6 Heater

The heat capacity 'C' is given by:

$$C = \frac{Q}{(\omega \mid T_{ac} \mid)}$$

where Q is the heat flow during one cycle, ω is the frequency, and T_{ac} is an amplitude of temperature variation.

Absolute values can be obtained if T_{ac} values are measured for a specimen(s) of known specific heat, e.g. sapphire, and the slopes of the plots of $1/T_{ac}$ *vs.* frequency compared. However, the technique is most valuable for determining changes in heat capacity e.g. due to phase transitions, over a very small temperature range. Since the actual rise in temperature during a measurement is only milliKelvins the conditions may be described as stationary or quasi-adiabatic.

In the calorimeter, a small specimen of the order of 4×4×0.3 mm (maximum) for absolute values and 2×2×0.01 mm (maximum) for relative values is supported inside the furnace by two 25 μm thermocouple wires welded together and attached with a silver paste. Helium gas is introduced in the specimen cell to maximize heat transfer between the specimen and surroundings. For this measurement and that of thermal diffusivity, D, as will be discussed later, the thickness of the specimen must be less than the thermal diffusion length which is given by $(2D/\omega)^{1/2}$.

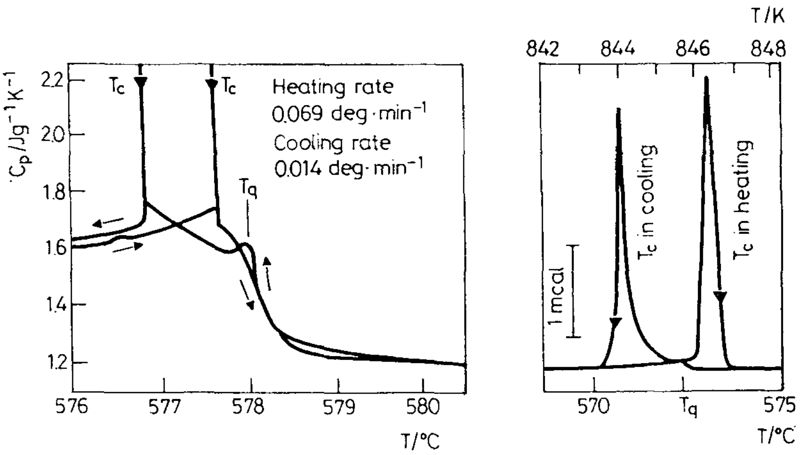

Fig. 3 Use of ac calorimeter technique to determine incommensurate transition

Overall the method has a sensitivity of some 10^2 to 10^3 higher than DSC and other analytical methods including adiabatic calorimetry [2]. One example of this precision is shown in Fig. 3 where the existence of an incommensurate phase of quartz has been detected between the α and β phases [3]. The ac calorimeter technique shown is Fig. 3a gives a very sharp peak for the α incommensurate transition, T_c, and another clear peak for the β-incommensurate peak (T_q) with a range of 1.15 K.

The method has been used for studies on a variety of polymer, ceramic, dielectric, semiconductor, and superconductor materials. It has been particularly valuable during the development of the YBCO type superconducting oxides at cryogenic temperatures [4].

Measurement of thermal diffusivity/thermal conductivity

For well over 20 years the well-known transitory temperature 'flash' method has been most widely used to measure this property on all types of solid homogeneous materials [5]. The specimen is a small, flat, 10–12 mm diameter, uniform disc having a thickness of 4 mm or less. The front face of the specimen is subjected to a short burst of radiant energy for lms or less. The temperature history of the rear surface is measured and the thermal diffusivity, D, computed from values of the half time (time to reach 50% of maximum) and square of thickness. Other percentage times can be used depending on the analytical model [6]. With certain modifications it can also be used to measure specific heat on the same specimen.

The technique, while revolutionary, is again not a panacea for all applications. The most common problem has been that of the mistaken application of deriving the thermal conductivity, λ, directly from the relationship relating D to λ, specific heat, C_p, and density, ρ. This relationship holds only for homogeneous materials, where the prime mode of heat transmissions is by solid conduction. For inhomogeneous, layered, and anisotropic materials and where radiation occurs special care needs to be applied both in the measurement and interpretation of results using special analyses.

In general, the method has been used to determine absolute values of thermal diffusivity in order to derive λ. However, it has been found very useful for a number of quantitative applications. In particular, during the development of different high thermal conductivity ceramics such as AlN. Figure 4 illustrates how the thermal conductivity of AlN can be increased significantly by the addition of Y_2O_3 to reduce the oxygen content [7].

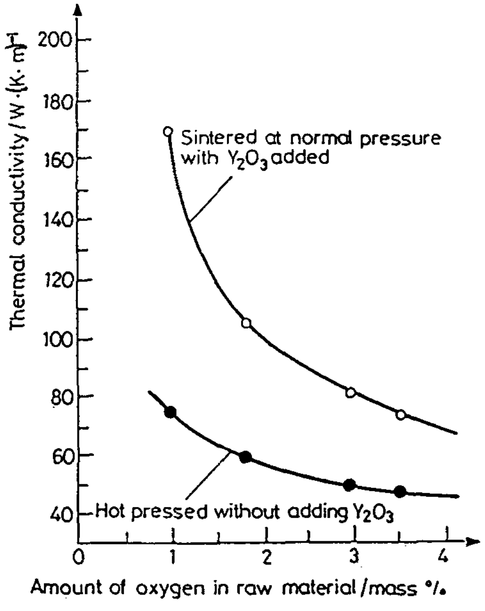

Fig. 4 Effect of O_2 impurity in AlN raw material and thermal conductivity of sintered AlN

However, one modification that we have developed recently [8] has been found particularly valuable for studying the uniformity and homogeneity of thin wafers such as silicon or ceramics produced for electronic components. It is based on a two-dimensional analysis and larger specimens than normally used (10–12 mm diameter) can be evaluated.

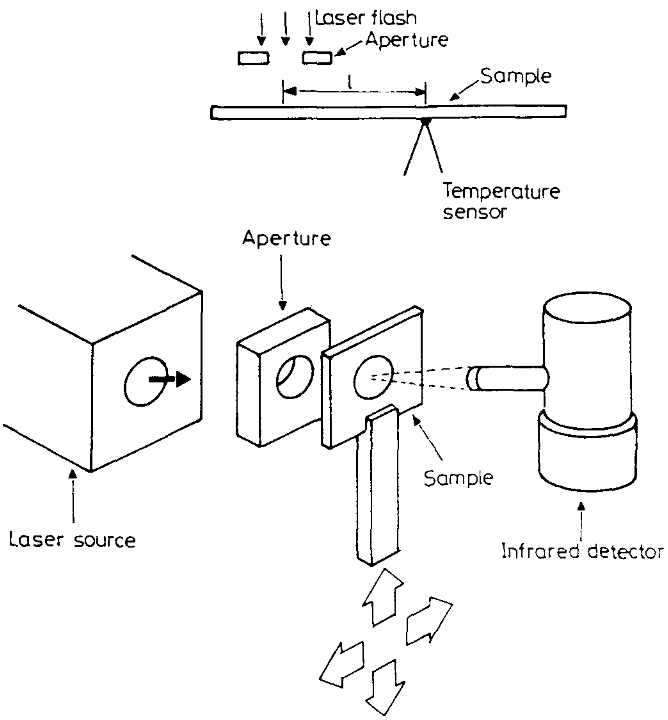

Fig. 5 Thermal diffusivity measurement on an infinite plate

The principle is illustrated in Fig. 5. The temperature history at point r, off-centre, can be derived analytically by assuming that the specimen is an infinite plate, that the thickness is very much less than the distance r, and that there are no heat losses. Although the analysis indicates it is possible to derive an absolute value for thermal diffusivity the technique appears to have more potential when used in a comparative mode by using a standard specimen(s) of known properties.

A second method developed to measure much thinner specimens including layered composites is a modification of the ac calorimeter discussed earlier [9]. The essential features are similar and the optimum specimen size is a film 10×4 mm with a maximum thickness of 0.35 mm. However, only part of the surface is subjected to the periodic thermal energy; the remainder is masked from the chopped light irradiation. The ac temperature at a position of the specimen under the mask is measured as in the ac calorimeter. The thermocouple does not affect the accuracy [10].

The thermal diffusivity, D, in the direction parallel to the surface to the specimen is obtained by measuring the ac temperature, T_{ac}, as a function of distance x between the position of the sensor and the edge of the mask. In the instrument, the mask is moved with respect to the fixed specimen.

The relation $|T_{ac}|$ *vs.* x is given by:

$$|T_{ac}| = \frac{Q\exp(-kx)}{2\omega c\, l}$$

where Q is the amplitude of the applied energy flux for unit area, ω is the angular frequency of the periodic heating, c the heat capacity of the specimen, l the specimen thickness, and k is the thermal decay constant $(\omega/2D)^{1/2}$ or $(\pi f/D)^{1/2}$ where f is $(\omega/2\pi)$ the ac frequency. D can thus be obtained from the decay constant. The specific heat is determined separately on the same specimen.

In practice, to ensure uniformity of heat flow, the front surface of the specimen is coated with a very thin layer of carbon, bismuth or some other highly-energy-absorbent material. This is particularly necessary for transparent materials. It has been demonstrated analytically and experimentally that effects of such layers less than 100 nm thick can be neglected even on specimens 10 µm thick [11].

Measurements can be carried out in air on many materials. However, for very thin films (< 25 µm) of very low diffusivity materials, e.g. polymers, it has been found preferable to undertake measurements in vacuum [12]. In such cases the conduction effect of the fluid layer in immediate contact with the specimen surface can become significant. If measurements are undertaken in air, the results are

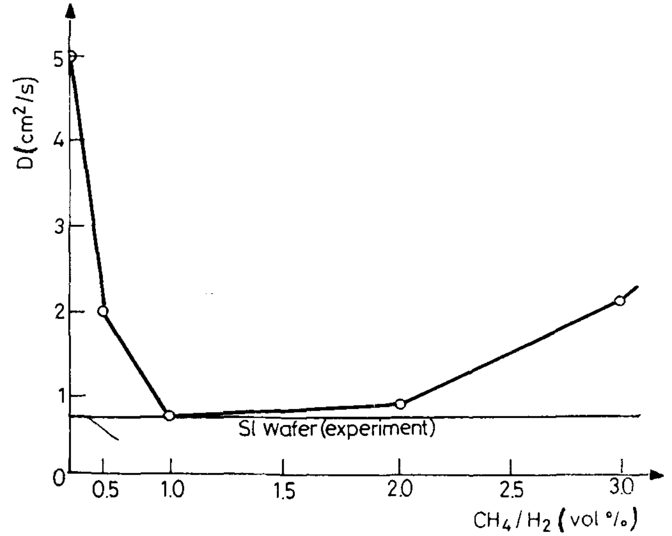

Fig. 6 Influence of methane concentration upon thermal diffusivity of diamond film

best analyzed in terms of a composite layer consisting of the specimen plus an air layer having a thickness proportional to the air diffusion length.

The method is valuable for evaluating the properties of all types of materials in the form of free-standing films and of composit layers consisting of a film and supporting substrate by use of a simple two-layer analysis.

Based on current experience, reliable results are possible providing $\lambda_1 l_1 \geq \lambda_2 l_2$. Measurements are still possible but with decreasing precision as $\lambda_1 l_1$ approaches $0.1\lambda_2 l_2$. Work is now underway using a laser as the energy source to see if the precision can be improved and the limit reduced below 0.1.

The method has been particularly useful for studying the effect of processing parameters on the thermal properties of diamond and the degree of homogeneity of films. In one investigation the effects of methane concentration on the properties of the diamond film were studied. In this silicon wafers 95 ± 10 μm thick were coated with plasma CVD diamond films from 5 to 30 μm thick. The results, shown in Fig. 6, indicate that the methane concentration has a significant effect on the crystallinity of the diamond. The crystalline structure becomes closer to that of the diamond (very high thermal diffusivity) as the concentration is decreased. Values for derived thermal conductivity of approximately 1000 W/mK were obtained for the specimen produced with the lowest methane concentration.

It should also be pointed out that thermal diffusivity and thermal conductivity are very sensitive to structure differences. Thus, the evaluation technique is not only useful for evaluating the effects of processing but also can be used for studying the existence of local variations of film quality over larger areas of a specimen.

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Zusammenfassung — Es wird das Prinzip und die Arbeitsweise eines Infrarot-"gold image furnace" diskutiert und seine Vorteile gegenüber herkömmlichen Widerstandsöfen zur Untersuchung von neuentwickelten Materialien beschrieben. Die Anwendung eines "gold image furnace" in Verbindung mit einem Standardmikroskop erlaubt eine kontinuierliche Beobachtung des Materiales bis zu sehr hohen Temperaturen. Es werden auch neue Wege zur Messung von Wärmekapazität und thermischer Diffusivität/Konduktivität beschrieben.