

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISI3N DE NUEVAS CREACIONES

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(Apoderado)

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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	Actuaci3n	430
	Oficio	N3 1 3 7 1 2
	Folios	022

Patente de Invenci3n	☒	Patente de Modelo de Utilidad	☐
V3a Nacional	☐		
V3a PCT (fase nacional)	☐	Cap. I	☐
		Cap. II	☐
Solicitud Internacional n.3			
Fecha de Presentaci3n Intrnl.			

Como resultado del examen de fondo, realizado con fundamento en el articulo 45 de la Decisi3n 486 de la Comisi3n de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- | | |
|-------------------------------|--|
| 1.1 <u>Descripci3n</u> : | Folios 3 a 12 como se radic3 inicialmente |
| 1.2 <u>Reivindicaciones</u> : | Folios 12 a 15 como se radic3 inicialmente |
| 1.3 <u>Dibujos</u> : | Folios 22 a 24 como se radic3 inicialmente |

2. Objeto de la invenci3n

- T3tulo de la solicitud: *M3todo y celda para la determinaci3n de la difusividad t3rmica de materiales durante [el] proceso de transferencia de calor por conducci3n, con r3pidos cambios de temperatura, que pueden incluir cambio de fase*, folio 1.
- El objeto de la presente solicitud de patente de invenci3n consiste en suministrar una celda (y un m3todo) para determinar confiablemente la difusividad t3rmica de los termopl3sticos sometidos a r3pidos cambios de temperatura, incluyendo el caso cuando hay cambios de fase, bajo condiciones similares a las que se encuentran en procesos industriales.

Reivindicaciones 1 a 19: Una celda de medición, semejante a un molde de inyección para la fabricación de una placa, que comprende: dos bloques metálicos (internos) removibles e intercambiables que están dotados de un sistema de enfriamiento y calentamiento, con una cavidad formada entre ellos, aislada (por medio de un espacio de aire) lateralmente de unos cuerpos que los sujetan, lo que restringe la transferencia transversal de calor del material en la cavidad por la presencia de dos barras poliméricas instaladas en sus bordes laterales, todo lo cual permite generar un rápido régimen de transferencia de calor unidimensional en la zona central de la placa del material a analizar; un conjunto de sensores de presión y de temperatura, que están instalados en forma fija en los cuerpos de la celda y están conectados a un sistema de adquisición de datos para el almacenamiento de las señales; **caracterizada** porque tiene un dispositivo removible, reparable y reutilizable, denominado unidad removible de sensores de temperatura, que posee tubos cerámicos o metálicos ensamblados en un bloque portador, para guiar y fijar un grupo de mínimo tres sensores de temperatura en la cavidad, conectados también al mismo sistema de adquisición de datos, para generar las curvas de calentamiento cuando la celda de medición se opera a alta temperatura con su sistema de calentamiento.

Reivindicaciones 20 a 23: Un método; para obtener a partir de un mínimo de tres señales de temperatura (tripleta) generadas durante el proceso rápido de enfriamiento o calentamiento por conducción para tres puntos igualmente espaciados en la dirección de flujo de calor de un cuerpo, como las obtenidas con la celda definida arriba; curvas de valores de la difusividad térmica del material del cuerpo bajo estudio, **caracterizado** porque estos valores satisfacen la ecuación diferencial discretizada para un flujo de calor no estacionario unidimensional por conducción, tal como se utiliza normalmente en programas de computador para la simulación de estos procesos de transformación.

El problema planteado en esta solicitud es satisfacer la necesidad de obtener valores de la difusividad térmica que se ajusten a los reales cuando el material bajo estudio sufre bruscos cambios de temperatura, y eventualmente de fase, tal como sucede en los procesos industriales.

Para solucionar este problema técnico la solicitud en estudio proporciona una celda que está dotada de una unidad removible de sensores de temperatura que permite acceder a una posición interna del material fundido o en proceso de fusión.

- Clasificación Internacional de Patentes (IPC) asignada: G01N 25/18

3. De la solicitud de Patente

3.1 Descripción (artículo 28 D. 486)

- Durante el análisis del texto de la descripción y de las ilustraciones anexadas, se observaron los siguientes defectos:
 - 1) El título o nombre de la invención tiene unos defectos menores: *Método y celda para la determinación de la difusividad térmica de materiales durante [el] proceso de transferencia de calor por conducción, con rápidos cambios de temperatura, que puede[n] incluir cambio de fase.* El primero: hace falta el artículo

determinado *el* antes de *proceso*. El segundo: faltan las comas para encerrar la expresión *con rápidos cambios de temperatura* y, el tercero: sobra la *n* en *pueden*, porque es el *proceso de transferencia de calor* el que puede incluir cambios de fase, no los *rápidos cambios de temperatura*, como se insinúa.

- 2) Tanto dentro de la descripción como dentro de las reivindicaciones se observaron membretes (esto es, encabezamientos y pies de página) que contienen información no pertinente respecto a la invención en sí. El solicitante debe presentar el capítulo descriptivo y el capítulo reivindicatorio libres de toda información irrelevante.
- 3) En la página 2, folio 4 de la descripción aparece el título **2. DESCRIPCIÓN** que no es pertinente en este momento ya que la parte 1, folios 3 y 4 también forma parte de la descripción. Una objeción similar se hace respecto al título 2.3 **DESCRIPCIÓN** que aparece en la página 4, folio 6.
- 4) En la misma página 2 aparece la expresión *grados Kelvin* que no es correcta, porque la unidad respectiva son los *kelvin*, sin grados.
- 5) En la misma página 2, hacia el final, aparecen citados varios documentos que requieren una aclaración respecto a si se trata de documentos de patentes o qué clase de documentos son.
- 6) En la página 3, folio 5, aparece la expresión *30 a 40 K/min* en donde hace falta especificar las unidades de la primera cantidad: *30 K/min a 40 K/min*.
- 7) En la Tabla 1, folio 10, aparecen mencionadas diversas variables de las cuales se ignoran las unidades, que deberían estar especificadas en cada caso.
- 8) En la página 8, folio 10, aparece la expresión *182.3 bar* en donde, en primer lugar, no se emplea la coma decimal, de uso obligatorio en Colombia, y, en segundo lugar no se emplean las unidades del Sistema Internacional (pascal, Pa).
- 9) En la figura 1, folio 21, se omitió señalar los números 24 y 29, a pesar de que, aparentemente, los detalles correspondientes sí están ilustrados.
- 10) En la figura 2, folio 22, aparece un número 29 sin la correspondiente flecha indicadora.
- 11) En la figura 5, folio 23, se omitieron los números de referencia. Todos los detalles que hayan sido numerados en alguna de las figuras y aparezcan en otra, deberán, en lo posible, aparecer señalados en todas las figuras en donde se encuentre ilustrado el detalle correspondiente. Por lo demás, si no se va a decir nada respecto de una figura en particular, es preferible omitirla.
- 12) En las figuras 8 y 9, folio 24, se omitió mencionar las unidades que corresponden a cada eje de las gráficas ilustradas, así como se omitió señalar las cantidades correspondientes a los puntos más significativos (los del cruce de las líneas de las cuadrículas con los ejes vertical y horizontal).

- La descripción no cumple con los requisitos de claridad y divulgación completa, lo que dificulta o impide su comprensión y ejecución de acuerdo al art. 28 de la Decisión 486.

3.2 Reivindicaciones (artículo 30 D 486)

- Durante el análisis del texto de las reivindicaciones se observaron los siguientes defectos:
 - 1) El capítulo reivindicatorio tiene membretes, objetados arriba con relación a la descripción.
 - 2) En la reivindicación 1, folio 1, aparece la expresión *calor transversal* cuyo significado, según el contexto, se desconoce.
 - 3) En la misma reivindicación 1, aparece la expresión *unidad removible de sensores de temperatura que posee tubos cerámicos o metálicos* cuyo contenido técnico no se encuentra en el capítulo descriptivo, por lo que esta reivindicación carece de soporte.
 - 4) Lo reclamado en las reivindicaciones 2 a 7, 9 a 11 y 14 a 19, folios 12 a 14, no tiene el debido soporte dentro del capítulo descriptivo.
 - 5) Lo reclamado en la reivindicación 12, folio 13, es redundante respecto a lo reclamado en la reivindicación 1, de la que depende; por consiguiente, afecta negativamente la concisión que debe tener el capítulo reivindicatorio. El solicitante debe desistir de esta reivindicación 12.
 - 6) Las reivindicaciones 20 a 23, folio 15, reclaman, todas, un método, pero ninguna de ellas lo define. Método, según el Diccionario de la Real Academia Española (DRAE), es el *Modo de decir o hacer con orden*. Pero aquí no se establece qué etapas o pasos se deben seguir y, por supuesto, no se establece ningún *orden*. Las reivindicaciones 20 a 23 no definen los alcances de la protección que desea el solicitante.
- Las reivindicaciones no cumplen con los requisitos de definición, claridad, concisión o sustento por la descripción de acuerdo al art. 30 de la Decisión 486. Debe entenderse que las reivindicaciones dependientes de las reivindicaciones objetadas son, asimismo, objetadas, por razones análogas.

Se deben presentar, entonces, nuevos capítulos descriptivo y reivindicatorio, ambos completos, junto con un nuevo juego de dibujos, donde se hayan corregido todas las objeciones que se han hecho arriba. Esto con el fin de evitar -cuando solo se presentan algunas páginas sueltas corregidas- que el lector tenga que desplazarse desde un sitio a otro de la solicitud y luego regresar a donde estaba antes sin perder la ilación de la lectura, porque esto produce confusión y afecta negativamente la claridad de dichos capítulos.

4. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el Estado de la Técnica es la

Fecha de presentación de la solicitud nacional 03-02-10

- Se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud teniendo en cuenta la fecha indicada; y durante la búsqueda de anterioridades se encontraron los siguientes documentos, que forman parte del estado de la técnica más cercano al objeto de la solicitud:

n.º	Documento	Título	Fecha de publicación
D1	Patente US 3 570 302, cuyo inventor es Harold A. Sauer, quien le cedió sus derechos a la Bell Telephone Laboratories, Inc.	«Method of measuring thermal diffusivity»(Un método para medir la difusividad térmica)	1971-03-16
D2	Patente US 4 933 887, cuyos inventores son György Dankó e Itsván Czifka, quienes le cedieron sus derechos a la Budapesti Muszaki Egyetem	«Process and apparatus for the determination of thermo-physical properties»(Un procedimiento y un aparato para determinar propiedades termofísicas)	1990-06-12
D3	Patente US 5 224 775, cuyos inventores son Michael Rading, Brian K Hahn y Benjamin S. Crowe, quienes le cedieron sus derechos a la TA Instruments, Inc.	«Method and apparatus for modulated differential analysis»(Un método y un aparato para el análisis diferencial modulado)	1993-07-06
D4	Patente US 5 833 365, cuyos inventores son Lambert Stals, Luc de Schepper, Jean Roggen y Ward de Ceuninck, quienes les cedieron sus derechos al Interuniversitair Micro-electronika Centrum vzw y al Limburgs Universitair Centrum	«Method for local temperature sensing for use in performing high resolution in-situ parameter measurements»(Un método para detectar la temperatura local para emplearse en las medidas in-situ de parámetros de alta resolución)	1998-11-10

Se anexa la copia de las páginas pertinentes de estos documentos

NOTAS: No se realizaron las evaluaciones de los demás requisitos de patentabilidad, porque se hicieron algunas objeciones respecto a la definición, la claridad, la concisión y el sustento por la descripción de las reivindicaciones.

No obstante lo anterior, con base en los documentos detectados hasta el momento, no se preveen objeciones respecto a la novedad o el nivel inventivo del objeto de la solicitud.

5. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados negativamente por la falta de claridad de la descripción y las reivindicaciones y por la falta de definición, de sustento y de concisión de estas últimas.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a

pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el número 5.2, letra e), del capítulo quinto del título primero de la Circular Única n.º 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha
13 0 OCT. 2008

CONCEPTO TÉCNICO n.º 3094	EXAMINADOR TÉCNICO Código n.º 202009
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March 16, 1971

H. A. SAUER

3,570,302

METHOD FOR MEASURING THERMAL DIFFUSIVITY

Filed Sept. 20, 1968

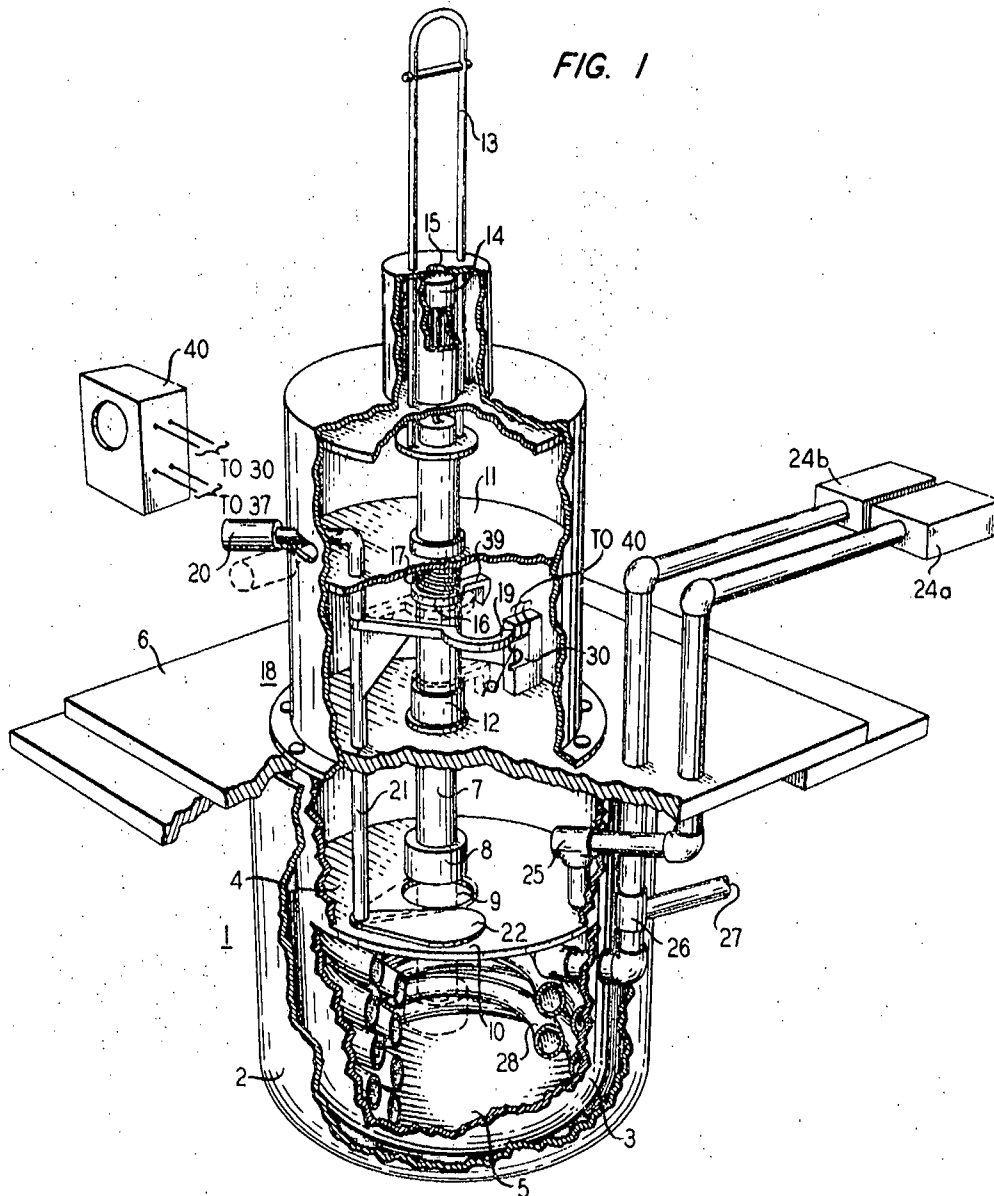
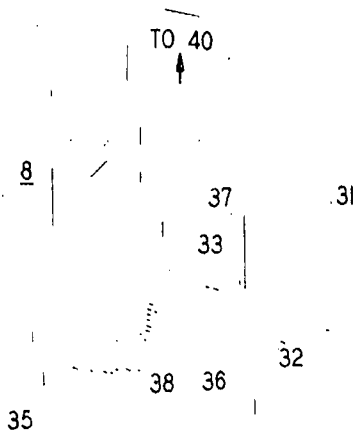


FIG. 2



INVENTOR
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BY *Charles E. Graw*

ATTORNEY

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3,570,302

METHOD FOR MEASURING THERMAL DIFFUSIVITY

Harold A. Sauer, Hathboro, Pa., assignor to Bell Telephone Laboratories, Incorporated, Murray Hill and Berkeley Heights, N.J.

Filed Sept. 20, 1968, Ser. No. 761,214

Int. Cl. G01n 25/00, 25/18

U.S. Cl. 73-15

4 Claims

ABSTRACT OF THE DISCLOSURE

The thermal diffusivity and specific heat of materials in thin sections is measured at low and moderate temperatures by a transient heat flow method which employs a sample probe and a dual chamber vessel. A small diameter sample is held on the probe, which is supported in the upper chamber. After the sample has been equilibrated at a chosen temperature, it is quickly lowered, mechanically, through a trap into contact with a liquid in the lower chamber, which is isolated from the upper chamber, and which is maintained at a different temperature. The lowering is conducted in such a manner that only the under or near surface of the specimen is brought in contact with the liquid. The temperature-time history of the far surface, obtained from a thermocouple attached to the center of this surface, is recorded on an oscilloscope.

FIELD OF THE INVENTION

This invention relates in general to measurement of thermal diffusivity. In particular, the invention concerns a method for calculating precisely from thermal diffusivity measurements the thermal conductivity of thin material specimens such as printed circuit board substrates and the like, the thermal conductance of thin composites, and the real or apparent specific heat.

BACKGROUND OF THE INVENTION

As printed circuit modules and integrated circuit packages become ever smaller in size, the need to know with precision the thermal conductance characteristics of the substrates on which these circuits are mounted has become quite critical. Often it is the ability to conduct and dissipate the heat generated by such circuits that determines the choice of substrate material and of composite substrate structures. As the limits of existing substrate materials and structures are approached, the search for alternatives with better heat conducting properties has required improved techniques of the aforementioned thermal diffusivity measurements.

In the past, the procedure for the direct measurement of thermal conductivity of thin, i.e., .003-.080 inch, elements of material involved a comparative technique in which the thin specimen was sandwiched between thermodes of known thermal conductivity. The principal problems with this approach to thermal conductivity measurement are the difficulty of establishing good physical and thermal contact of the specimen to the thermodes and the uncertainty in the determination of the temperature gradient across the specimen. To circumvent these difficulties investigators turned to the measurement of thermal diffusivity from which with a knowledge of the density and specific heat of the specimen, the thermal conductivity is calculated.

Current thermal diffusivity techniques for thin specimens involve either the application of heat pulses from laser beams or flash lamp sources, or the application of modulated electron beams. Inherently, with both these heat wave methods, the experimental techniques are complicated and the measurements are time consuming and

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difficult to effect. Moreover, they are oriented toward high temperature measurements in which duration of energy pulse and radiation losses from the impinging surface have introduced additional complications in the procedure and in the mathematical expressions for calculating thermal diffusivity. Further, since the sample, in these techniques, is exposed to an evacuated environment during measurement, temperature conditioning and control in the below-ambient region is difficult to achieve in the same experimental set-up as is employed for the above-ambient measurements.

Accordingly, one object of the invention is to measure accurately and speedily the thermal diffusivity and specific heat of thin material sections, especially in the low and moderate temperature range.

Another object of the invention is to facilitate the search for materials for printed circuit substrates.

A broader object of the invention is to realize an alternative to existing thermal conductivity measurement techniques for all categories of thin materials.

SUMMARY OF THE INVENTION

In accordance with the invention, thermal conductivity measurements on a thin element are achieved by establishing a stable temperature differential between two thermally isolated but contiguous chambers, placing the substrate on a probe in the upper chamber until the probe is temperature stabilized, and then quickly injecting the probe and substrate through a trap between chambers and into contact with a temperature-controlled liquid in the second chamber.

The resulting time-temperature history of the far surface, as measured at its center provides the necessary and sufficient information for calculating the thermal diffusivity. At the same time, it provides the necessary and sufficient information for calculating the specific heat when compared with the time-temperature response of a sample of material of known specific heat of the same geometry and under the same test conditions.

In a specific embodiment of the invention, a printed circuit board substrate shaped in the form of a thin disc is provided with an evaporated gold plating on the far surface. To this a thermocouple is attached as by ultrasonic bonding. The substrate is housed at the end of a metallic probe. With the use of gaseous heat exchange carriers, such as nitrogen, the respective temperatures of the two contiguous chambers are established and their differential, say, of 25 degrees C., is carefully maintained. Once the probe and substrate are also temperature stabilized in the upper chamber, the probe is rapidly lowered through a trap into the second chamber, with only its near surface making contact with the liquid bath therein.

A flow of heat between the liquid and the substrate occurs, and a change of current is generated in the thermocouple. This change of current reflects a change in temperature of the far surface in the direction of the near surface. Advantageously, this signal is applied for example, to the vertical trace of an oscilloscope, the horizontal input being time triggered by contact of the substrate with the liquid. Since a considerable change in temperature in these thin elements occurs in less than a second, it is desirable to photograph the time-temperature trace. The magnitude of change in unit time, all other parameters being maintained constant, is a function of the differential cryostat-thermostat temperature.

A principal feature of the inventive method, accordingly, involves the use of two contiguous thermal chambers whose temperatures are carefully controlled by gas heat exchange media, and a probe which rapidly transports a thin measurement specimen from one to the other, the temperature change being measured by thermocouples.

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An added feature of the invention is the synchronization of the movement of the probe and trap door, which enables the rapid relocation of a specimen from one chamber to a second without significant heat loss during this procedure.

The invention, its further objects, features, and advantages may be readily apprehended from a reading of the description to follow of an illustrative embodiment thereof.

DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective frontal view of a preferred item of apparatus which practices the invention; and

FIG. 2 is a front detail view of the plunger cap, substrate, and thermocouple assembly.

DETAILED DESCRIPTION OF AN ILLUSTRATIVE EMBODIMENT

Although the inventive embodiment about to be described relates specifically to thermal diffusivity measurements on a thin specimen, it will be obvious that the method and equipment alike are applicable to any materials of variable thickness provided that the boundary conditions required by theory can be met; and, accordingly, to specific heat and thermal conductivity determinations as well.

THERMODYNAMICS OF THE METHOD

The problem of measuring thermal diffusivity of a thin specimen by this method resolves analytically into measuring the temperature change at the far surface of a specimen due to a sudden and dramatic change in temperature at the near surface. This change stems from unidirectional flow of heat through a specimen which has plane parallel faces of separation thickness l . The heat flow is considered to be normal to these faces. The sample is brought to some initial equilibrium temperature. At time $t=0$, the near face, at $x=0$ is brought in contact with a heat source or sink which is at a constant temperature. The other or far face (at $x=l$) is assumed to be perfectly insulated at all times except from the thermal effects of the near face. A flow of heat commences in the direction of the dimension l .

The classical differential equation for unidirectional heat transfer by conduction in a medium in which the temperature is changing with time is given by:

$$\frac{\partial \theta}{\partial t} = D_H \frac{\partial^2 \theta}{\partial x^2} \quad (1)$$

At a time $t>0$, the temperature of the specimen face opposite the liquid contacting face has reached a value θ .

Given the following set of boundary conditions:

$$t=0, \theta=0$$

$$t>0, \theta=\theta' \text{ at } x=0$$

$$t>0, \frac{\partial \theta}{\partial x}=0 \text{ at } x=l$$

θ and θ' being in degrees C., the mathematical form of the solution of Equation 1 is:

$$\theta = \sum_{N=0}^{\infty} (-1)^N \theta' \cdot 2 \cdot \operatorname{erfc} \frac{(2N+1) \cdot l}{2\sqrt{D_H \cdot t}} \quad (2)$$

where θ is the temperature of the distant face, and θ' is the temperature of the near face, choosing a temperature scale where the initial temperature is everywhere zero.

$$\frac{\theta}{\theta'} = \sum_{N=0}^{\infty} (-1)^N \cdot 2 \cdot \operatorname{erfc} \frac{(2N+1) \cdot l}{2\sqrt{D_H \cdot t}} \quad (3)$$

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If only the first term, $N=0$, of the series is considered, Equation 3 becomes

$$\frac{\theta}{\theta'} = 2 \operatorname{erfc} \frac{l}{2\sqrt{D_H \cdot t}} \quad (4)$$

In the measurement of the thermal diffusivity by the experimental methods to be described below, it is convenient to let

$$D_H = D_1 \cdot \frac{l^2}{t} \quad (5)$$

Thus Equation 4 reduces to

$$\frac{\theta}{\theta'} = 2 \operatorname{erfc} \frac{1}{2\sqrt{D_1}} \quad (6)$$

The significance of Equation 6 is that both θ/θ' and D_1 are dimensionless quantities. Accordingly, for arbitrarily chosen values of θ/θ' , a value of D_1 can be computed for each value of θ/θ' . Experimentally this means that if θ/θ' is chosen as a parameter of the test prior to the measurement, the corresponding value of D_1 becomes a parameter of the test Equation 5. Since the thickness l of the sample is known, the value of the thermal diffusivity, D_H , is determined from the time, t , required for the far face to change in temperature by an amount which satisfies the ratio θ/θ' .

EXEMPLARY APPARATUS

A preferred example of a facility for the practice of the inventive method is depicted in FIG. 1 which shows an overall thermal diffusivity measuring facility, which might appropriately be termed a cryostat-thermostat. Cryostat-thermostat 1 consists of an outer shell 2, and an inner shell 3. The latter consists of an upper chamber 4 and a lower chamber 5, which is thermally isolated from chamber 4. The chambers 4, 5 are conveniently mounted to the underside of a plate 6 which could be positioned over a suitable laboratory recess, for example.

The assembly for manipulating a specimen to be tested consists of a probe 7 and a sample holder 8, the latter being shown in detail in FIG. 2. The probe assembly is suitably mounted for vertical movement within the apparatus; thus permitting movement of sample holder 8 through a trap 9 in the plate 10 which divides chambers 4 and 5. Probe 7 is vertically located by the guideplate 11 and the bushing 12 below it. A probe lifter 13 is attached to the top of probe 7 and emerges from the enclosure to serve as a means for raising the sample holder after a measurement has been conducted. A vacuum cylinder 14 and associated vacuum adjustment valve 15 provide a convenient routine adjustment for the rate of plunge of the probe 7.

To the probe 7 is attached a flange 16, and a loading spring 17 is engaged between the flange 16 and the underside of guideplate 11. A plunging and trap control assembly, designated 18, includes an arm 19 that engages the underside of flange 16, thus fixing the raised position of probe 7. In such position, sample holder 8 is fully within the upper chamber 4. The swivable control lever 20 rotates the linkage 21 to the trap door 22.

Door 22 is closed over the circular trap 10 while the chambers 4, 5 and the specimen are being temperature equilibrated. Rotation of the lever 20 first opens door 22 and then releases the probe flange 16, which permits the spring 17 to inject the probe and sample holder into lower chamber 5.

Advantageously, upper chamber 4 is temperature controlled by a gas, and chamber 5 contains a liquid 23 which is temperature controlled. Pursuant to the preferred construction of the present apparatus, gaseous heat carriers are employed for temperature control. Gas such as nitrogen from a first temperature-controlled source 24a is introduced into upper chamber 5 through the gas diffuser 25. Nitrogen gas from a second temperature-controlled source 24b feeds into lower chamber 5 through the gas

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diffuser 26 which also allows introduction of nitrogen gas at ambient temperature through inlet 27. The gas is circulated in lower chamber 5 through the cooling coils 28 and thereafter fed into diffuser 25. Drains for each of the chambers 4, 5, the thermocouples in these chambers which monitor the temperature therein and other associated routine apparatus are omitted from FIG. 1 for the sake of clarity.

As seen in FIG. 2, the sample holder 8 consists of a hollow cylindrical section 31 forming the end of probe 8, with an exterior threaded portion. The interior of section 31 is provided with a seat 32 into which an O-ring 33 fits. O-ring 33 is advantageously made of gold to withstand a wide range of possible temperatures.

PRACTICE OF THE THERMAL DIFFUSIVITY MEASURING METHOD

A thin specimen 40 such as shown in FIG. 2 is affixed to sample holder 8 and the latter is positioned in the upper chamber 4. Chamber 4 is brought to a conveniently chosen initial temperature equilibrium, which defines the reference temperature from which θ and θ' are calculated. Liquid 23 in lower chamber 5 simultaneously is brought to a fixed temperature, for example, chosen to be approximately 25 degrees C. higher or lower than the temperature in chamber 4. The gaseous heat carriers permit the establishment and control of a temperature difference between the two chambers over a wide temperature range stemming from well below ambient to well above.

The material specimen 34 is prepared by coating its far face 36 with evaporated gold and at the center attaching a thermocouple 37 with an ultrasonic or thermocompression bond, for example. Specimen 34 then is placed in seat 32 and a threaded cap 35 attaches to cylinder 31 to secure the specimen in the seat 32 against O-ring 33. The near side 38 of specimen 34 is exposed to the ambient outside of probe 7 which, in chamber 5, is the liquid 23. The interior and far side 36 are protected from any extraneous thermal disturbance other than that which originates on near side 38.

When the specimen 34 equilibrium is reached as indicated by thermocouple 37, the plunging and trap door control 20 is actuated manually, permitting the probe and sample holder to drop rapidly into lower chamber 5. Its travel is controlled to an amount just sufficient to enable the specimen near side 38 to contact the surface of liquid 23. At the moment that the near side 38 contacts the liquid surface, a transfer of heat is initiated through the sample. Simultaneously, a microswitch 30 is actuated by contact with the extension 39 of arm 19, which trips the horizontal sweep circuit of an oscilloscope 40. The synchronization of the onset of the heat transient and the oscilloscope's sweep pattern results in the reproducible recording of the signal provided by thermocouple 37. At the conclusion of the heat transient, probe 7 is lifted manually by lifter 13 back into the upper chamber 4, and the doors 22 are closed.

The liquid 23 preferably is of low viscosity and low surface tension over its useful temperature range to permit intimate contact to the near side 38 of specimen 34.

EXAMPLE

Suppose that it is desired to calculate D_H , the thermal diffusivity of a specimen, at a temperature of 200 degrees C. The initial equilibrium temperature in chamber 4 thus is 200 degrees C.; and the sudden change in tem-

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perature of near side 38 is conveniently selected as being from 200 degrees C. to 225 degrees C. Accordingly, liquid 23 is brought to a temperature of 225 degrees C. The specimen thickness l is 0.025 inch. The probe 7 is plunged and it is found that after 0.0125 second, θ (the temperature change occurring on far face 36) is 15 degrees C. in accordance with a predetermined ratio $\theta/\theta'=0.600$. The corresponding value of D_1 is 0.469. From Equation 5 D_H is calculated to be 0.15 cm.² per second. The temperature range of interest can be explored by raising or lowering temperatures of the chambers 4, 5 and repeating the operation.

The measurement techniques are amenable to a wide variety of substrate structures including, for example, unglazed ceramic such as alumina, beryllia and alkaline earth porcelains; to glazed ceramics and to vitreous enamel on metal. The techniques described are useful in studying the effects of thickness of glaze or enamel, nature of interfaces, devitrification or recrystallization in glaze or enamel, intimacy of contact between metal film and substrate, and power dissipated in resistance films.

In addition to its applicability to substrate material studies, however, the inventive method is also germane to composites such as layered structures, glass bonded mica plastic laminates and filled plastics; to metallized bonding layers on ceramics; and to ceramic-to-metal seals.

It is to be understood that the embodiments described herein are merely illustrative of the principles of the invention. Various modifications may be made thereto by persons skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for measuring thermal diffusivity between parallel top and bottom major surfaces of a thin specimen comprising the steps of:
establishing an initial stable temperature in the specimen by exposing same to gaseous heat exchange carriers;
thereafter rapidly bringing substantially all points on the bottom surface only, into intimate total and substantially simultaneous contact with a liquid stabilized and maintained at a temperature different from said initial temperature;
measuring the temperature of said top surface at its center as a function of time; while
precluding the lateral flow of heat at said specimen center during the measurement interval.
2. A method in accordance with claim 1, wherein said specimen thickness is in the range of 0.005 to 0.050 inch.
3. A method in accordance with claim 2, wherein said measuring step is commenced the instant said specimen contacts said liquid surface.
4. A method pursuant to claim 3, wherein the difference between the initial specimen temperature and the temperature stabilized liquid is of the order 25 degrees C.

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H. GOLDSTEIN, Assistant Examiner

United States Patent [19]

Dankó et al.

[11] Patent Number: 4,933,887

[45] Date of Patent: Jun. 12, 1990

[54] PROCESS AND APPARATUS FOR THE DETERMINATION OF THERMO-PHYSICAL PROPERTIES

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[52] U.S. Cl. 364/557; 374/5; 374/44; 374/136

[58] Field of Search 364/550, 551.01, 557; 374/5, 7, 43, 44, 136

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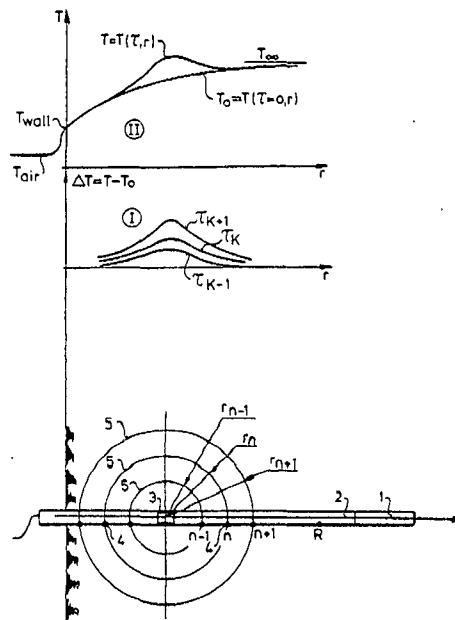
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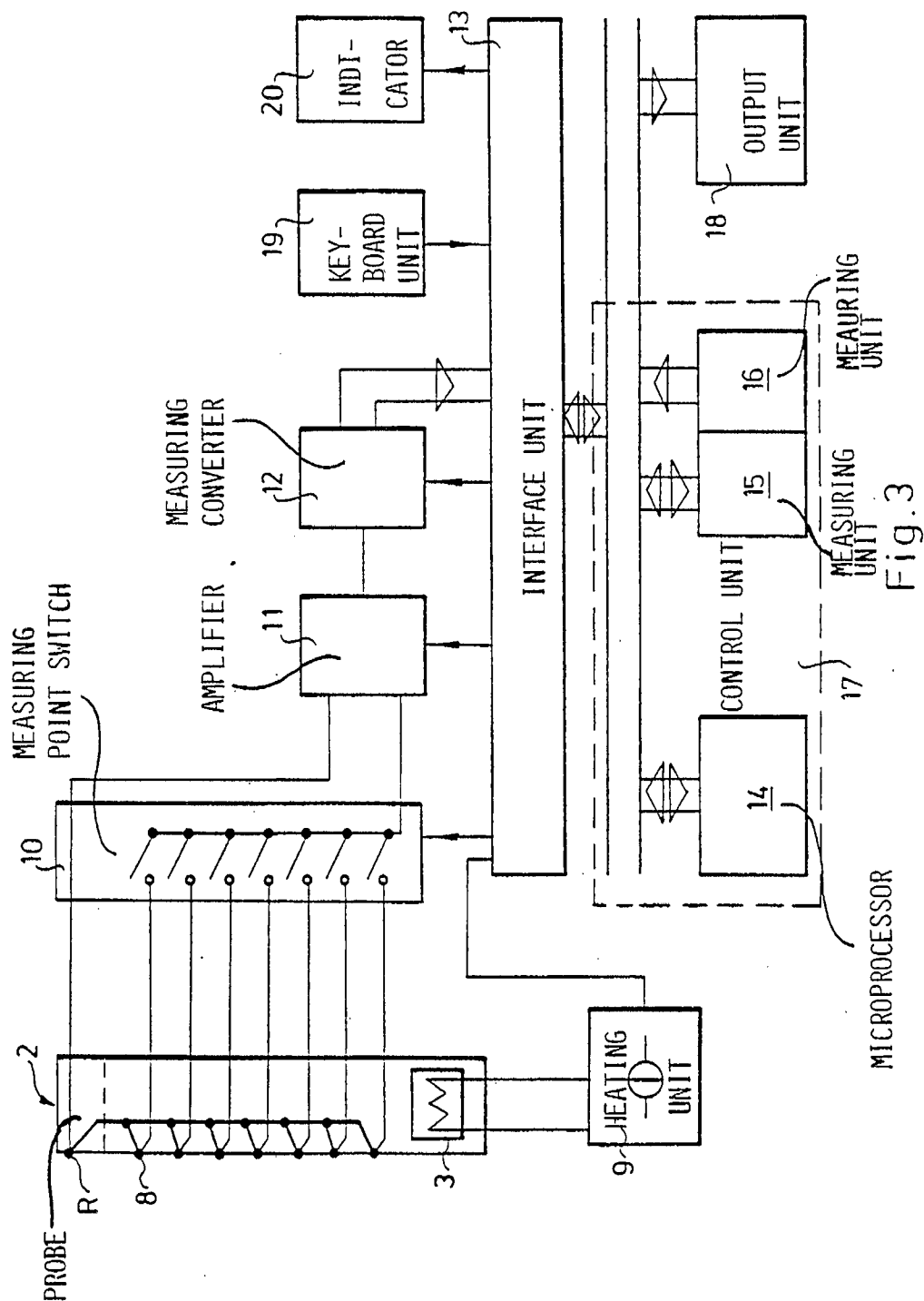
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[57] ABSTRACT

A process for the simultaneous, in-situ determination of thermophysical properties, primarily for determination of the thermal conductivity and thermal diffusivity, according to which in a certain volume of the material to be tested a temperature field varying with time is brought about by perturbation due to heating and this temperature field is measured, then certain properties are determined by calculation from the obtained temperature data and the known heating power input spherical isotherms are formed in the material to be tested in a way, that temperature change of at least one degree Celsius is brought about at the measuring points which are arranged along a straight line passing through the heat source and intersecting the isotherms along their diameter, and a measuring probe formed as a rod-type body made of poor heat conductive material having a heating element and measuring points, wherein the heating element is formed as a point-like heat source.

20 Claims, 4 Drawing Sheets





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examined and the testing depth is to be determined with regard to this. A cooling process, too, can be used by way of checking for the determination of thermal diffusivity "a".

The measuring apparatus required for the measuring process consists of probe 2 and the instruments for measurement, control and evaluation.

In a preferred embodiment of the invention, heating element 3 used in probe 2, contrary to the known solutions in the literature, is formed not as a linear but as a point-type heat source. Accordingly, the isothermic surfaces in the medium (in case of homogeneous testing material) will take a spherical shape instead of cylindrical surfaces.

For the determination of thermal diffusivity "a" the temperature changes with time observed at different measuring points 4 should be used. Evaluation of the measurement is based on matching the measured temperature change to the calculated values using the describing differential equation. With the use of three adjacent measuring points e.g. points $n-1$, n and $n+1$ corresponding to points r_{n-1} , r_n and r_{n+1} , as well as with the use of two consecutive points of time, e.g. points of time τ_k and τ_{k+1} shown in diagram 1, the solution of the differential equation derived from the Fourier differential equation does not require the application of separate boundary condition equation, or more exactly boundary condition of the first kind is used implicitly. Parameter "a" offering the best fitting can be considered as the final result of the measurement evaluation. The knowledge of the perturbing heat flux input is not required for the evaluation, hence the determination of "a" and λ is independent from each other.

Heating perturbation of such intensity is required for the measurement, which generates a well measurable, e.g. 10° C. temperature change within a few hours at the point of heating. Recording the temperature rise with time brought about by heating is required in several, but at least three times during measurement. Then the unknown properties should be determined by calculation from the temperature changes with time on the basis of the mathematical model of the temperature change brought about by the perturbation.

Heating element 3 which can be found about the centre of the probe, is an electric surface heating layer the length of which is approximately equal to its diameter whose own thermal capacity is low. For the sake of good contact with the surface of the tested material, the heating layer is formed as filament 7 mounted on elastic ring 6 as shown in FIG. 2. The elasticity of elastic ring 6 is ensured by a longitudinal slit.

The temperature sensors for measuring the spherical isotherms are spaced along the length of the probe. The measuring points 4 should be arranged at least in one direction moving away from the point-like source and with a view to simple evaluating calculation, in a uniform spacing. The sensors can be arranged also in both directions moving away from the point-like heat source and this allows of checking the spherical symmetry of the isotherms at least along one diameter. In the case of differences, the calculation can be corrected by averaging or by other ways. The surface temperature sensors should be fastened onto the surface similarly to fastening the heating layer. In the case of using elastic rings, the rings should be contracted when the sensors are inserted to prevent damage. Thermocouples can be used as temperature sensors, which are particularly suitable for measuring temperature differences. The

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difference formation is rendered possible by arranging the reference point R, i.e. the cold junction of the thermocouples in a point sufficiently far from the place of the heat source (such as 1 m), as undisturbed by the heater during measurement. It is possible to use several series connected thermocouples in each measuring point, the hot junctions of which are arranged in the respective measuring points, and the cold junctions in the reference point. In this way the measuring signal and the accuracy can be increased. The number of series connected thermocouples may vary at each measuring point and can be increased when moving away from the point-like heat source whereby relatively more intensive measuring signal can be obtained at the points where the temperature change is lower, and thus the accuracy can be increased.

A multi-channel, measuring data acquisition instrument or system of general purpose can be used for measuring, recording and evaluating the signals of the temperature sensors. In the course of measurement heating should be switched on (or switched off for the control measurement during cooling down), and for this purpose a supplementary heating unit is necessary which is synchronized with the measuring unit, i.e. controlled by the control unit. The block diagram of such instrument supplemented with heating unit is shown by way of example in FIG. 3.

The probe 2 according to the invention with the heating element 3 and thermocouples 8 forming the measuring points are shown on the left side of FIG. 3. Heating element 3 is connected with the heating unit 9 controlling the active thermal intervention. Thermocouples 8 are connected to the measuring point switch 10 with the help of which the temperature sensing thermocouple can be selected.

The microvolt size thermovoltages obtained during the measurement are amplified by 10^3 - 10^4 order of magnitude with the help of amplifier 11. Measuring converter 12 is connected to amplifier 11, which is an analog-digital measuring converter and forms the numerical values of the measured voltage.

An interface unit 13 ensures the connection between the peripheries and the central unit. A control unit 17 formed by measuring units 15 and 16 as well as a microprocessor 14 is connected to the interface unit 13. The memory areas RAM and ROM of measuring units 15 and 16 are suitable for the storage of measuring data, as well as the measuring control and evaluating computational programs.

Output unit 18 can be connected to the control unit 17. Control unit 17 can be the central unit of a computer.

The instrument also includes a keyboard unit 19 and an indicator 20 for the display of the final results.

A measuring process is introduced by way of example as follows:

Measurements were performed in the andesitic rock of a mine. About 1 m deep hole was drilled into this rock for the probe of the measuring system.

The surface heat flux density ensured by the heating element used in the probe was $q = 10^4$ W/m², the radius of the heating element formed as point-type heat source was $R = 0.02225$ m, the length $l = 0.05$ m.

The measuring points are spaced along the probe as follows:

$r(m) = 0.0225; 0.1; 0.125; 0.15; 0.175; 0.2; 0.225; 0.25; 0.275; 0.3; 0.325; 0.35; 0.375; 0.4; 0.425; 0.45; 0.475; 0.5; 0.525; 1.0.$

The measurements were performed at the following time intervals: τ (s)=226; 450; 900; 1800; 3600; 5400; 7200; 9000; 10 800; 12 600; 14 400; 16 200; 18 000; 19 800; 21 600; 23 400; 25 200; 27 000; 28 800.

The set of curves shown in diagram I are obtained during the measurement. According to the given measurement results it is evident that at the point of time of the last measurement i.e. at the 8.5th hour, the radius of the penetration depth, i.e. the perturbed area is about 1 m. Hence it follows that the reference point should be arranged beyond this distance.

The temperatures of the curves belonging to the first few points of evaluation since the perturbation has not enough penetration depth, hence it is advisable to start the evaluation in the 2nd hour.

The value of the max. temperature rise in the first measuring point on radius $r=0.0225$ m was 80.9° Kelvin at the last measuring point of time.

It is advisable to perform the evaluation in the middle part of the temperature field. This is shown in FIG. 4, which is the set of curves matched to the measured temperature distribution.

Between temperatures $T_{n-1,k}$, $T_{n,k}$ and $T_{n+1,k}$ obtained at three adjacent radii at the same time T_k and the temperature $T_{n,k+1}$ related to the next point of time at the middle position, the following difference equation can be derived from the descriptive Fourier differential equation of heat conduction:

$$T_{n,k+1} = \frac{2a\Delta\tau}{r^2} \left(\frac{T_{n+1,k} \cdot r_{n+1} + T_{n-1,k} \cdot r_{n-1}}{2} \right) - T_{n,k} \left(\frac{2a\Delta\tau}{r^2} - 1 \right) \quad (5)$$

From above equation it follows that the thermal diffusivity "a" can be calculated from four different temperature values ($T_{n,k+1}$; $T_{n+1,k}$; $T_{n-1,k}$ and $T_{n,k}$). Its value from the measurement was given as $a=10^6$ m²/s.

Since the temperature field of spherical isotherms function r and τ is known in the following form

$$T(r,\tau) = \frac{q \cdot R^2}{\lambda \cdot r} \cdot f(r,\tau)$$

thermal conductivity λ with the knowledge of "a" and heat flux density "q" can be recalculated from a single measured temperature. In this case, the value of the thermal conductivity was $\lambda=2.5$ W/mK.

It was shown that the calculation formulae of the temperature distribution could be used in reverse order during evaluation to calculate the unknown thermophysical properties. However, it is advisable to perform several evaluations then averaging; method of the least squares fit can be used during this work.

The examples demonstrate that the process according to the invention, in the course of which point like heat source is used and accordingly, spherical isotherms are obtained in the medium, is suitable for the determination of different thermophysical properties, C.e. for determination of heat conductivity and thermal diffusivity independently from each other within a single measuring period. The measurement is extremely simple, but it needs a sophisticated measuring apparatus. The inaccuracies due to model-error occurring during evaluation

can be kept at a low level. Consequently, the process and the probe can be used well for in-situ measurements.

We claim:

1. A process for the in situ determination of thermophysical properties of a solid material, primarily for determination of thermal conductivity and thermal diffusivity in a certain volume of a solid, stationary material to be tested, comprising the steps of making a hole in said material, inserting into said hole in said solid stationary material a probe having a number of temperature sensors and a heat source, generating a temperature field varying with time with said heat source by way of driving with a known heating power input, measuring the temperature field at a plurality of measuring points on the inside surface of said hole in the material to generate temperature data for said plurality of measuring points, said sensor being in intimate contact with said material at said measuring points whereby the space for convection currents in said hole is minimized and measurement may be taken substantially without the interference of convection currents, determining selected properties by calculation from said temperature data and the known heating power input, wherein said point-like heat source is used in contact with said material for heating to form substantially spherical isotherms in a perturbed portion of the material to be tested to induce a measurable temperature change at the measuring points, said measuring points at different distances from the heat source being arranged along a straight line passing through the heat source and intersecting the isotherms along their diameter, wherein the measuring points are selected so that the maximum size of the point-like heating element is substantially smaller than the distance between the point-like heating element and the farthest measuring point.

2. A process as in claim 1, wherein a constant heat flow density is used for generating said spherical isotherms.

3. A process as in claim 1, wherein the measurements are performed at least at two consecutive points of time.

4. A process as claimed in claim 1, wherein measurements are performed at three or more measuring points.

5. A process as claimed in claim 1, wherein measurements are performed for a maximum of 10 hours.

6. A process as claimed in claim 1, wherein the measurements are performed at points substantially in a line which extends from the point-like heat source along the length of said hole to the entry point of said hole into said material.

7. A process as claimed in claim 1, wherein measurements are performed at points disposed in a line along the length of said hole, the point-like heat source being positioned between each of said opposite hole ends and measurement being performed at points between said source and one of said ends of said hole and at points between said source and the other of said ends of said hole.

8. A process as in claim 7, wherein said points are disposed at symmetrical positions with respect to said point-like heat source and wherein the temperature of a reference point is measured, said point being outside the perturbed temperature field.

9. A measuring probe for the simultaneous in situ determination of thermophysical properties, primarily for determination of the thermal conductivity and thermal diffusivity in a large volume of a solid stationary material, comprising a rod-like body made of poorly heat conductive material, a heating element formed as a



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United States Patent [19]
Reading et al.

[11] **Patent Number:** **5,224,775**
 [45] **Date of Patent:** **Jul. 6, 1993**

- [54] **METHOD AND APPARATUS FOR MODULATED DIFFERENTIAL ANALYSIS**
- [75] **Inventors:** Michael Reading, London, England; Brian K. Hahn, Newark; Benjamin S. Crowe, Centerville, both of Del.
- [73] **Assignee:** TA Instruments, Inc., New Castle, Del.
- [21] **Appl. No.:** 844,448
- [22] **Filed:** Mar. 2, 1992
- [51] **Int. Cl.⁵** G01N 25/00
- [52] **U.S. Cl.** 374/11; 374/33; 374/43
- [58] **Field of Search** 374/10, 11, 12, 13, 374/14, 16, 31, 33, 43

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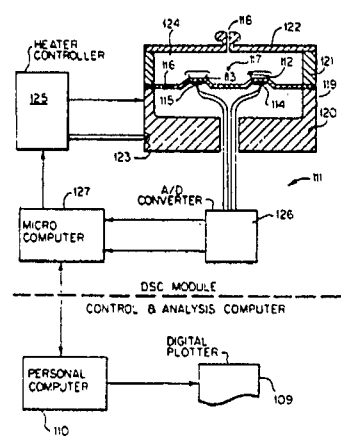
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[57] **ABSTRACT**

The present invention relates to differential analytical techniques for determining the composition, phase, structure, identification or other properties of a material that undergoes a transition as function of a driving variable. As applied to differential scanning calorimetric analysis (DSC), the preferred embodiment comprises: (1) heating a sample of the material with a linear temperature ramp that is modulated with a sinusoidal heating rate oscillation; and (2) deconvoluting the resultant heat flow signal into rapidly reversible and non-rapidly reversible components.

55 Claims, 9 Drawing Sheets



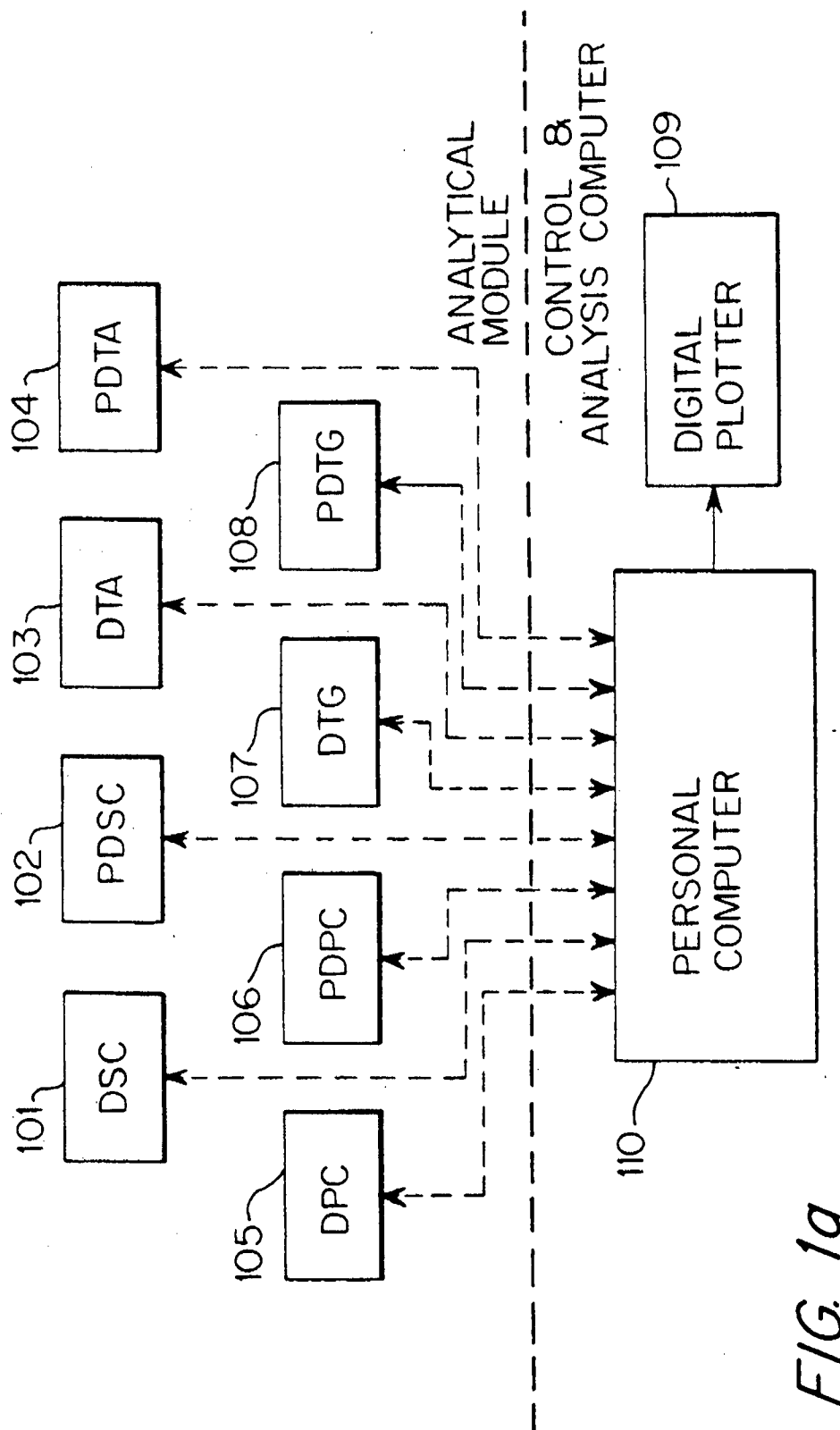


FIG. 1a

METHOD AND APPARATUS FOR MODULATED DIFFERENTIAL ANALYSIS

BACKGROUND

1. Field of the Invention

The present invention relates to differential analytical techniques for determining the composition, phase, structure, or other properties of a sample of material.

2. Background of the Invention

Thermal analysis techniques generally comprise measuring a physical parameter as a function of the temperature of the sample. The sample temperature is strictly controlled throughout the analysis. Whenever the sample undergoes a chemical transformation, a physical transformation, a phase change or another transition which affects the physical parameter being measured, the changes in that physical parameter may be interpreted to analyze the composition, structure, or thermal stability of the sample.

In differential thermal analysis techniques, the physical parameter of the sample being measured is compared to that of a reference, as a function of the temperature of the sample. The difference in the physical parameter measured for the sample and that measured for the reference is then recorded. The differential thermal analysis technique compensates for the effects of heating rate and ambient conditions that could cause changes in the measured physical parameter of the sample and reference. The differential thermal analysis technique can increase the sensitivity of the measurement of the physical parameter by removing large offsets in the value of the physical parameter whenever the precision of the measuring apparatus is limited.

One common thermal analysis technique is Differential Scanning Calorimetry (DSC). DSC is a thermal analysis technique which measures the temperatures and heat flow associated with chemical or physical transitions in materials as a function of time and temperature. The classical DSC method comprises heating the sample material and the reference material at a constant rate of temperature increase, typically 5° C. to 20° C. per minute, and recording the difference in heat flow into or out of the sample and the reference as a function of temperature.

Other differential thermal analysis techniques include Pressure Differential Scanning Calorimetry (PDSC), Differential Thermal Analysis (DTA), Pressure Differential Thermal Analysis (PDTA), Differential Photocalorimetry (DPC), pressure Differential Photocalorimetry (PDPC), Differential Thermogravimetry (DTG), and Pressure Differential Thermogravimetry (PDTG).

Furthermore, the present invention applies to all differential analysis techniques. It is not limited to differential thermal techniques. Whereas thermal differential analysis techniques depend upon temperature as the driving variable, non-thermal differential analysis techniques depend upon another driving variable, such as pressure, applied stress, or wavelength of incident radiation.

DSC measurements provide quantitative and qualitative information about the sample transitions that involve endothermic or exothermic processes, or changes in heat capacity. Pressure DSC is a related technique in which the heat flow and temperature of transitions are measured as a function of temperature under controlled

pressure, or as a function of pressure under controlled temperature.

Differential Thermal Analysis, like DSC, measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. However, unlike DSC, DTA results are semi-quantitative. Pressure DTA is a related technique in which the heat flow and temperature of transitions are measured as a function of temperature under controlled pressure, or as a function of pressure under controlled temperature. DTA is generally carried out at higher temperatures than DSC.

Differential Photocalorimetry measures the heat absorbed or released by a sample as it and a reference are exposed simultaneously to radiation of known wavelength and intensity. Pressure DPC is a related technique in which the heat absorbed or released by the sample is measured as a function of temperature under controlled pressure, or as a function of pressure under controlled temperature.

Differential Thermogravimetry measures the differential weight change of a sample and a reference as a function of time and temperature. Pressure DTG is a related technique in which the differential weight change is measured as a function of temperature under controlled pressure, or as a function of pressure under controlled temperature.

High resolution analytical techniques are described in U.S. patent application Ser. No. 07/638,847. That application is incorporated by reference herein. Those techniques seek to improve the resolution of changes in a characterizing physical parameter by controlling the rate of sample heating during transitions as a function of the rate of change of the physical parameter. When non-differential thermal analysis techniques are used, the high resolution techniques are effective in improving resolution for many transitions. However, they usually reduce the sensitivity of transitions when applied to differential thermal analysis techniques. This is because, for most differential thermal analysis techniques, the magnitude of the differential physical parameter is a direct function of the heating rate. Reducing the heating rate during transitions causes the differential signal to change, which may alter or obscure the true differential signal resulting from the transition event. This obscuring of the physical parameter can reduce the utility of the high resolution techniques when applied to conventional differential thermal analysis techniques.

Conventional differential thermal analysis techniques are limited in their ability to separate non-reversible events caused by enthalpic processes (chemical or physical) from reversible events such as changes in the heat capacity of the sample. This is because the reversible and non-reversible processes often occur simultaneously, or occur severely overlapped in time and/or temperature.

In addition, conventional and high resolution thermal analysis techniques cannot distinguish between rapidly reversible and non-rapidly reversible transitions within a single heating or cooling scan of the sample.

DEFINITIONS

"Transition" or "Transformation", as used herein, mean any type of physical or chemical transformation, phase change, or structural change in a material.

"Analyzing", as used herein with respect to materials, means determining the composition, phase, structure, and/or identification of the material.

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"Driving variable", as used herein, means the independent physical parameter, such as temperature, pressure, applied stress, or wavelength of incident radiation, that is being used to drive a material through a transition. For example, in thermal analysis techniques such as DSC, temperature is typically the driving variable.

"Characterizing differential physical parameter", as used herein, means the dependent differential physical parameter characterizing the sample, such as its heat flow, weight change, or change in dielectric or mechanical properties.

"Rapidly reversible", as used herein, means any portion of a signal, transition, or event which is a direct function of the rate of change of the driving variable. For example, the contribution to the heat flow signal in DSC attributable to the rate of change of temperature of the sample material is a rapidly reversible transition. In DSC, for example, one of the contributions to the rapidly reversible portion of the heat flow signal is the heat capacity of the sample material. Rapidly reversible processes include those processes which are thermodynamically reversible and can occur rapidly relative to the rate of change of the driving variable.

"Non-rapidly reversible", as used herein, means any portion of a signal, transition or event which is a direct function of the value of the driving variable. For example, the contribution to the heat flow signal in DSC attributable to the absolute temperature of the sample material is a non-rapidly reversible transition. This might be caused by a chemical or physical change taking place such as recrystallization. Non-rapidly reversible processes include those processes which are thermodynamically irreversible, as well as processes which are thermodynamically reversible, but which reverse very slowly relative to the rate of change of the driving variable due to the kinetic limitations of the process.

"Deconvolution", as used herein, means the process of separating the dependence of a characterizing physical parameter on a driving variable into two or more component parts so that the component parts can be utilized or analyzed separately, or compared with each other. For example, the dependence of a characterizing physical parameter can be deconvoluted into rapidly reversible and non-rapidly reversible components.

"Signal baseline", as used herein, means that portion of a signal representing the value of a characterizing physical parameter obtained in a range in which there are no transitions or transformations.

"Sensitivity" of an analytical technique, as used herein, means the degree to which signals associated with transitions can be physically distinguished from the signal baseline in the analytical data produced by the technique. This quality of the analytical technique is most critical when the value of the driving variable is changing very slowly.

"Resolution" of an analytical technique, as used herein, means the degree to which signals associated with different transitions can be physically separated in the analytical data produced by the technique. This quality of the analytical technique is most critical when multiple transitions occur at closely spaced values of the driving variable.

"Moving averaged", is a data smoothing technique that can be applied to data collected as discrete data points at uniform increments, comprising averaging the raw data over a window of n data points to obtain a single smoothed data point, incrementing the window by one data point, and repeating the process until all the

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data has been averaged. Thus the first n raw data points, data points $i=1, \dots, n$, are averaged to calculate the first smoothed data point, data points $i=2, \dots, n+1$, are averaged to produce the second data point, etc.

A "pulse wave" is a wave of spikes or impulse functions occurring at regular intervals. As applied to thermal analysis techniques, a pulse wave could be produced by bursts of instantaneous energy, e.g., from a laser, at regular intervals. The key characteristic of a pulse wave is that the duration of the energy burst is short compared to the duration of its effect.

SUMMARY OF THE INVENTION

In modulated DSC (MDSC), a rapid heating rate oscillation is added to a conventional linear temperature ramp. If the heating rate oscillation has low amplitude but high frequency then it is possible to obtain a relatively high instantaneous heating rate even though the underlying heating rate is comparatively low.

The present invention uses a computer system to control a differential thermal analytical technique by monitoring and modulating the technique's driving variable and deconvoluting a resultant characterizing differential physical parameter into rapidly reversible and non-rapidly reversible contributions.

For example, when the analytical technique is DSC, the driving variable is temperature and the characterizing differential physical parameter is heat flow. The response of the calorimeter to the sample can be expressed as follows:

$$dQ/dt = -dT/dt \cdot f_r(t, T) + f_n(t, T) \quad (1)$$

Where

dQ/dt = heat flow out of the sample (Joules/sec)

dT/dt = heating rate ($^{\circ}\text{C./sec}$)

t = time (seconds)

T = temperature ($^{\circ}\text{C.}$)

$f_r(t, T)$ = rapidly reversible contribution (Joules/ $^{\circ}\text{C.}$)

$f_n(t, T)$ = non-rapidly reversible contribution (Joules/sec)

$f_r(t, T)$ and $f_n(t, T)$ are functions of time and temperature derived by deconvolution of the analytical data.

This equation separates the DSC differential heat flow into a rapidly reversible portion, $f_r(t, T)$, which is dependent on heating rate, and a non-rapidly reversible portion, $f_n(t, T)$, which is not dependent on heating rate.

The modulated DSC heat flow signal will contain a heat flow oscillation which will be to some degree out of phase with the heating rate oscillation. The modulated DSC heat flow signal can be deconvoluted to separate the rapidly reversible, $f_r(t, T)$ and non-rapidly reversible, $f_n(t, T)$, heat flow contributions, as shown in equation (1).

Deconvolution of the modulated DSC heat flow and temperature data into parameters other than the ones described above is also possible. For example, the modulated heat flow and temperature data could be deconvoluted to derive direct kinetic information about the sample, such as its reaction rate and activation energy.

Other useful properties which could be deconvoluted include the heat capacity of the sample and the phase shift between the modulated sample heating rate and the resultant heat flow.

The modulated DSC technique can be further extended to automatically or manually vary the modulation frequency and/or amplitude during the DSC scan so as to obtain data at multiple frequencies, amplitudes



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United States Patent [19]
Stals et al.

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[45] Date of Patent: Nov. 10, 1998

[54] METHOD FOR LOCAL TEMPERATURE SENSING FOR USE IN PERFORMING HIGH RESOLUTION IN-SITU PARAMETER MEASUREMENTS

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[73] Assignees: Interuniversitair Micro-Electronika Centrum vzw; Limburgs Universitair Centrum, both of Belgium

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[21] Appl. No.: 620,250
[22] Filed: Mar. 22, 1996
[30] Foreign Application Priority Data

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[51] Int. Cl.⁶ G01N 25/72
[52] U.S. Cl. 374/5; 374/43
[58] Field of Search 374/1, 4, 5, 43, 374/45, 57, 181; 324/703; 364/571.03

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Attorney, Agent, or Firm—McDonnell Boehnen Hulbert & Berghoff

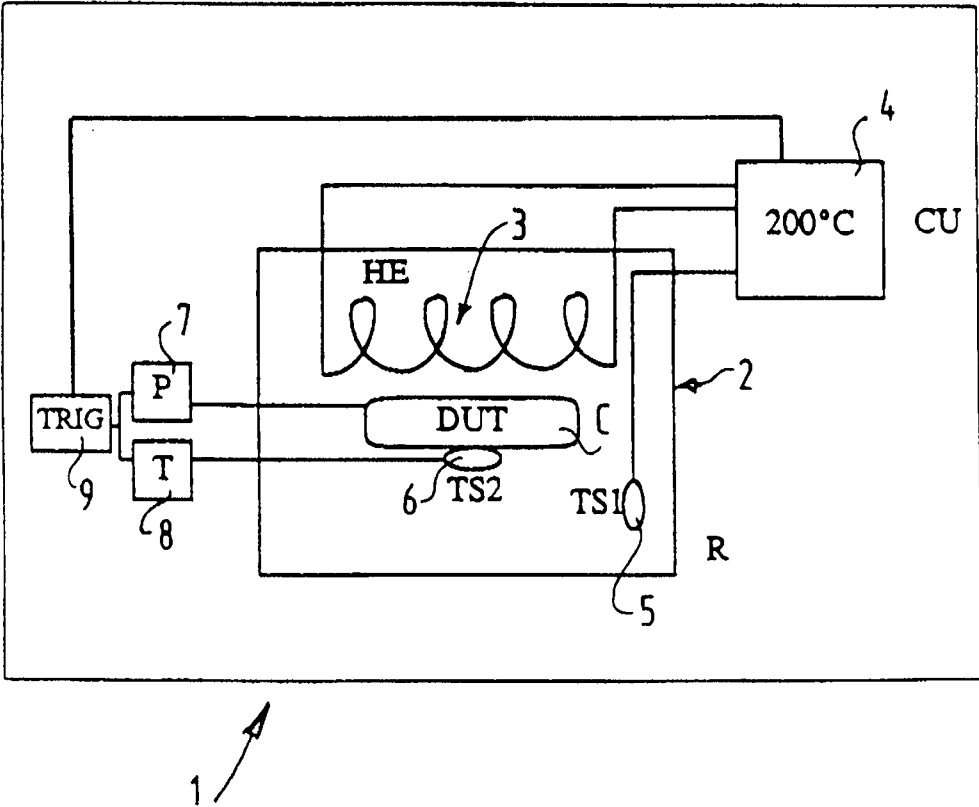
[57] ABSTRACT

An apparatus and method for measuring a parameter of a sample or component at a measurement temperature, wherein the parameter and the measurement temperature are measured at substantially the same time. A temperature coefficient of the sample or component is also established by using temperature fluctuations measured at or near the sample at the time at which the parameter is measured. The temperature coefficient is used to correct the measured parameter data and enhance its stability.

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6 Claims, 7 Drawing Sheets



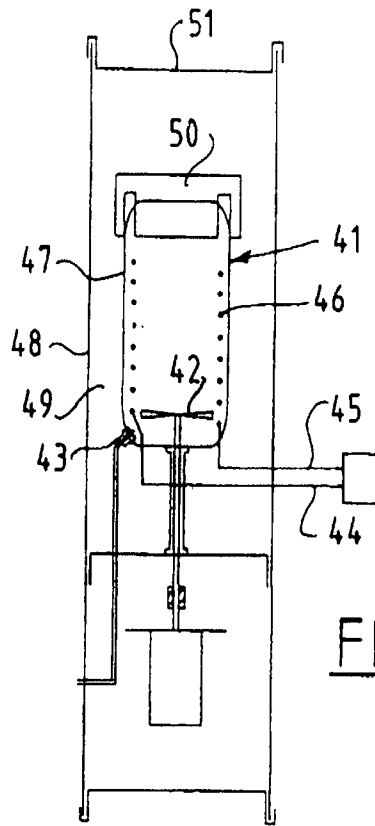


FIG. 7

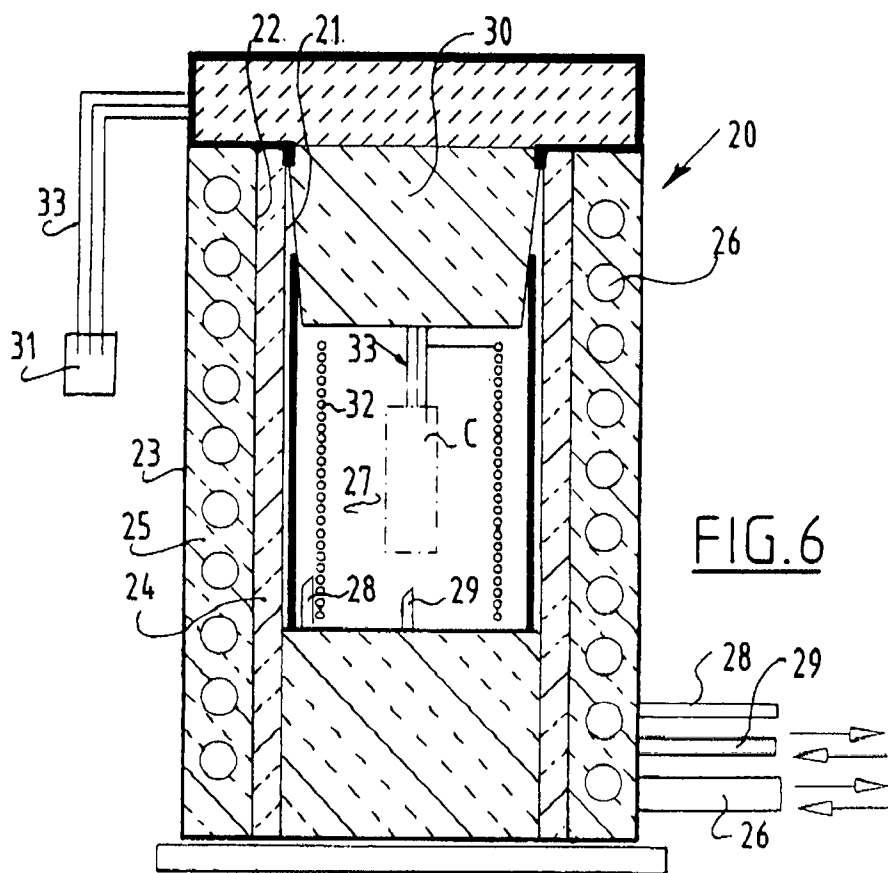


FIG. 6

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METHOD FOR LOCAL TEMPERATURE SENSING FOR USE IN PERFORMING HIGH RESOLUTION IN-SITU PARAMETER MEASUREMENTS

BACKGROUND OF THE INVENTION

The reliability of electronic components is of crucial importance in modern industry. There is an increasing demand for realistic predictions of the lifetimes of electronic components and of the variation of the components' parameter values over their lifetimes. The components of interest for such parameter value predictions include diodes, transistors, passive components such as metalization lines, wire bonds, resistors, capacitors, dielectrics, etc.

One method for predicting the value of a component's ageing parameter as a function of time is to place the component in an environment having an elevated temperature, perform a measurement of the parameter, and then repeat the cycle until sufficient measurements are made to permit a reliable prediction of the parameter value over time. However, because of the time required to perform this method it is particularly disadvantageous for systems wherein a small change of the parameter value occurs.

In European Patent Application EP-A-0395149, an in-situ component ageing technique is described, wherein it is possible to measure a component parameter value at an elevated temperature during a relatively short time period, typically on the order of 48 hours or less. In such a case, it is necessary that experimental errors in the collected data be minimized if extrapolation of the results to real operating conditions and future times are desired. In this technique, the oven in which the elevated temperature is achieved has a high temperature stability, e.g. on the order of $\pm 0.01^\circ \text{C}$., or even as small as $\pm 0.001^\circ \text{C}$.

Such a high degree of temperature stability is difficult to achieve and is sometimes accomplished by limiting the physical size of the oven, which generally permits better control of the temperature distribution within the oven. However, a disadvantage of limiting the physical size of the oven is that only one or a small number of components can be evaluated at the same time.

What is desired is an apparatus and method for obtaining high precision measurements of a component parameter which are corrected for temperature fluctuations occurring in an oven in which the measurements are made.

SUMMARY OF THE INVENTION

The present invention provides a method for measuring a property or parameter of a sample at a certain measurement temperature, wherein the property and the measurement temperature are determined at substantially the same point in time. In addition, a temperature coefficient of the sample is established based on temperature fluctuations measured at or near the sample at that point in time. The temperature coefficient is used to correct the measured property value and assist in evaluating the variation of the measured property over time.

According to a further aspect of the present invention, there is disclosed an oven or furnace in which such reliability tests and parameter measurements can be conducted.

Further details, advantages and features of the present invention will become clear upon reading the following description with reference to the annexed drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram of a preferred embodiment of an apparatus for implementing the local temperature sensing and high resolution measurement method of the present invention.

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FIG. 2 is a data plot showing the temperature difference within the apparatus and the effective corrected temperature difference for parameter measurements made using the apparatus of FIG. 1.

FIG. 3 is a more detailed representation of the corrected temperature data shown in FIG. 2.

FIG. 4 is a data plot showing the temperature fluctuations (ΔT) as a function of time within a box-oil-bath furnace when operated at a temperature of $T=150^\circ \text{C}$.

FIG. 5 is a data plot of the effective temperature variation for the data shown in FIG. 4 after correction in accordance with the method of the present invention.

FIG. 6 is a sectional view of a first oven or furnace suitable for use in performing the method of the present invention.

FIG. 7 is a sectional view of a second oven or furnace suitable for use in performing the method of the present invention.

FIG. 8 is a sectional view of a third oven or furnace suitable for use in performing the method of the present invention.

FIG. 9 is a schematic view of a fourth oven or furnace suitable for use in performing the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 is a block diagram of a preferred embodiment of an apparatus 1 for implementing the local temperature sensing and high resolution measurement method of the present invention. In apparatus 1 of the present invention, an electronic component C (labelled "DUT", device under test in the figure) is arranged in a recipient or oven 2 which is provided with heating means 3 (labelled "HE"). Heating means 3 are connected to a control unit 4 (labelled "CU") to which a first temperature sensor 5 (labelled "TS1") placed inside furnace 2 is also connected. Near the component C a second temperature sensor 6 (labelled "TS2") is arranged. Temperature sensor 6 is arranged so as to be in good thermal contact with component C. Component C is connected to a multimeter circuit 7 (labelled "P") for measuring the desired ageing parameter or property of the component. Second temperature sensor 6 is connected to a second multimeter circuit 8 (labelled "T") for acquisition of data regarding the temperature of the component. Both multimeter circuits 7 and 8 are connected to the same trigger circuit 9 (labelled "TRIG"), which is also connected to control unit 4. By triggering multimeter circuits 7 and 8 at the same time, a file with the information (P,T,t) is produced and stored, wherein t is the time of the measurement, T is the temperature measured by second temperature sensor 6, and P is the property or parameter of the component measured.

As will be described, the collected data (P,T,t) is subsequently processed to enhance the stability of the data set. This reduces the variance of the data contained in the data set. The processing causes the performance level (in terms of ability to accurately predict the value of the measured parameter over time) of the corrected data set to be better than, or at least comparable to that which can be obtained using a furnace with higher temperature precision (less variation of the temperature inside the oven). The data processing method of the present invention will now be described.

The temperature dependence of an electrical parameter P, i.e., P(T) can be expressed as:

$$P(T) = P(T^*) \cdot (1 + \alpha \Delta T) \quad [1]$$

where α is the temperature coefficient of the component with respect to the measured parameter, T^* is the desired temperature at which the parameter value is to be determined, T is the temperature measured by sensor 6 (the temperature of, or in close proximity to the component placed in the oven), and ΔT is the difference between the temperatures T and T^* (i.e., $T - T^*$). Equation [1] describes a linear relationship (expressed in terms of α) between the parameter value at one temperature and its value at a second temperature. Note that a more general relationship between $P(T^*)$ and $P(T)$ can also be used when practicing the present invention, with any changes to the steps to be described being within the capabilities of one skilled in the art.

If a set of data files (P_i, T_i) is available, where $i = 1..N$, then assuming α is known, a corrected data set can be calculated using the following relationship:

$$P^c(T^*) = P(T^*) \quad (\text{from equation 1}) = P(T) / (1 + \alpha(T - T^*)) = P(T) \cdot (1 - \alpha(T - T^*)) \quad [2]$$

Equation 2 is applicable under the assumption that $\alpha(T - T^*) \ll 1$, which is the case for the systems and measurement conditions typically encountered. Note that this assumption is useful for facilitating the mathematical formulation of the method and is not required for practice of the method. $P^c(T^*)$ is the calculated value of the parameter P at the desired temperature T^* , referred to as $P(T^*)$ in equation 1.

The temperature coefficient α can be determined from the (P, T) data sets by using a minimalization procedure. A number of mathematical methods are suitable for this purpose.

When using the method of Cook (B. C. Cook, Physical Review, No. 106, page 300, 1957), wherein a smoothness parameter S is defined in relation to the calculated data, the optimum value of α for maximum smoothness is determined as follows:

$$\alpha = \frac{\sum (P_{i+1} - P_i) \cdot (P_{i+1} \Delta T_{i+1} - P_i \Delta T_i)}{\sum (P_{i+1} \Delta T_{i+1} - P_i \Delta T_i)^2}$$

$$S = \sum (P_{i+1}^c - P_i^c)^2$$

In the equation for α , ΔT_i is the i th value for the temperature difference ($T - T^*$) obtained from the (P_i, T_i) data file. Note that other more complex smoothness parameters can of course be used for processing the data. By virtue of the above equations, it is shown that the temperature coefficient (α) can be determined using the measured (P, T) data. It is significant to note that the presence of temperature fluctuations, ΔT , are used to determine the quantity α . Once the temperature coefficient is determined, it is inserted into equation [2] to determine the corrected value of the component parameter. The corrected value corresponds to the parameter value which would be obtained by performing the parameter measurement in an oven having an enhanced temperature stability compared to the oven in which the measurements were actually performed.

The minimalization procedure can be performed on sections of the (P, T) data set, and not on the entire data set simultaneously. In this way a temperature coefficient (α) curve as function of ageing time can be obtained. This formulation of the quantity α can be introduced in the temperature stability enhancement routine described by the previous equations by making α a function of time. This

leads to a more complex mathematical formulation than the one described above for determining $P^c(T^*)$. This technique will be referred to as the Δ - α deconvolution technique, since it is possible to discriminate between drift of the component parameter values ΔP , and temperature coefficient (α) characterization during ageing as a result of a single isothermal ageing experiment. Apart from the possibility that changes in the process occur during ageing, the above technique is also useful for theoretical studies and verification purposes. Note that the temperature coefficient (α) of a temperature sensor itself may be calculated and used to correct the temperature measurements made within an oven or furnace used to measure the parameter data.

It has been shown by the inventors of the present invention that the above described concept further enhances the effective temperature stability of the measured P data. This means that the processed (P, T) data has a variance in the parameter values which corresponds to that which would be obtained from making the parameter measurements in a "high precision" oven having a higher degree of temperature stability. Precision furnace systems make use of multimeters with a temperature read-in resolution of approximately $\pm 0.0002^\circ \text{C}$. When using the above described parameter data correction concept it becomes possible to correct the data to have an effective temperature stability that equals this amount. However, in accordance with the present invention, it is possible to achieve the noted performance level with a furnace system that has a temperature stability of in the range of only $\pm 0.5^\circ \text{C}$. As a result, the inventive concept can reduce costs and make parameter ageing determinations less sensitive to environmental fluctuations of temperature and other parameters.

A further beneficial feature of the described invention is the ability to measure the parameters of a number of components at the same time in a medium precision furnace with high capacity, such as a classic box-oven. Due to the high volume capacity of such a system when used with the data correction method described, it is possible to achieve a high level of temperature stability and/or uniformity for a number of components simultaneously, in a manner comparable to that of a high precision furnace. In such an embodiment of the present invention, every component will be equipped with an individual temperature sensor. Many measurements can be conducted at the same time with a high degree of accuracy and stability, even in the case where the local temperature in the oven varies.

FIG. 2 is a data plot showing the temperature difference ΔT within the apparatus and the effective corrected temperature difference ΔT_{corr} (expressed in $^\circ \text{C}$) as a function of measurement time (expressed in seconds) for parameter measurements obtained using the apparatus of FIG. 1. The scattered points in the figure (ΔT) represent the temperature fluctuations within the apparatus as measured at the active zone near a component. As indicated by the spread of the data, a temperature stability of approximately $\pm 0.05^\circ \text{C}$ is present. The points lying on a flat line (corresponding to a value of 0.00°C) result from using the previously described algorithm to correct the parameter measurements. These points (ΔT_{corr}) represent the effective temperature fluctuations corresponding to the corrected parameter data. In FIG. 3 (and FIG. 2) it is shown that the ΔT_{corr} data points have an effective temperature stability of approximately $\pm 0.0005^\circ \text{C}$. This value is an improvement by a factor of 100 over the temperature fluctuations actually present in the oven, as represented by the scattered data of FIG. 2. For this example, this means that by using the apparatus and method of the present invention, parameter measurements can be obtained which have a temperature stability on the order of 100 times