MEASURING SEEBECK COEFFICIENT

Inventor: G. Jeffrey Snyder, Pasadena, CA (US)

Assignee: California Institute of Technology, Pasadena, CA (US)

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 601 days.

App. No.: 13/403,835

Filed: Feb. 23, 2012

Prior Publication Data
US 2012/0213250 A1 Aug. 23, 2012

Related U.S. Application Data
Provisional application No. 61/445,937, filed on Feb. 23, 2011, provisional application No. 61/501,608, filed on Jun. 27, 2011.

Int. Cl.
G01K 7/00 (2006.01)
G01K 7/02 (2006.01)
G01N 25/32 (2006.01)

U.S. Cl.
CPC: G01K 7/02 (2013.01); G01N 25/32 (2013.01)

Field of Classification Search
CPC: G01K 7/02 (2006.01)
USPC: 374/179, E7.004

See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS
7,175,343 B2 * 2/2007 Phillips ................. 374/180

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

ABSTRACT
A high temperature Seebeck coefficient measurement apparatus and method with various features to minimize typical sources of errors is described. Common sources of temperature and voltage measurement errors which may impact accurate measurement are identified and reduced. Applying the identified principles, a high temperature Seebeck measurement apparatus and method employing a uniaxial, four-point geometry is described to operate from room temperature up to 1300K. These techniques for non-destructive Seebeck coefficient measurements are simple to operate, and are suitable for bulk samples with a broad range of physical types and shapes.

21 Claims, 10 Drawing Sheets
References Cited

OTHER PUBLICATIONS


* cited by examiner
FIG. 1
FIG. 5
Dispose a first heater assembly having a first bore therethrough exiting at a first substantially perpendicular surface to contact the sample and produce a first isothermal sample surface.

Dispose a second heater assembly having a second bore therethrough exiting at a second substantially perpendicular surface to contact the sample and produce a second isothermal sample surface on a sample side opposite the first isothermal sample surface.

Measure temperature of the first isothermal sample surface with a first thermocouple having a first axis where temperature and voltage are sensed at an end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface.

Measure voltage of the first isothermal sample surface with the first thermocouple.

Measure temperature of the second isothermal sample surface with a second thermocouple having a second axis where temperature and voltage are sensed at an end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface.

Measure voltage of the second isothermal sample surface with the second thermocouple; and calculating the Seebeck coefficient of the sample from the temperatures and voltages of the first isothermal sample surface and second isothermal sample surface.

Calculate the Seebeck coefficient of the sample from the temperatures and voltages of the first isothermal sample surface and second isothermal sample surface.

**FIG. 6**
MEASURING SEEBECK COEFFICIENT

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. §119 (e) of the following U.S. provisional patent applications, which are incorporated by reference herein:


STATEMENT OF GOVERNMENT RIGHTS

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to determining the Seebeck coefficient for thermoelectric materials. Particularly, this invention relates to measuring the Seebeck coefficient for high temperature thermoelectric materials.

2. Description of the Related Art

An applied temperature difference across a material causes charged carriers in the material (electrons or holes) to diffuse from the hot side to the cold side. Mobile charged carriers migrating from the hot to the cold side leave behind their oppositely charged and immobile nuclei, resulting in a thermoelectric voltage across the material.

The term, "thermoelectric," refers to the fact that the voltage is created by a temperature difference. Since a separation of charges also yields an electric field, the buildup of charged carriers on the cold side eventually ceases at some maximum value for a given temperature difference as there exists an equal amount of charged carriers drifting back to the hot side as a result of the electric field equilibrium. An increase in the temperature difference can result in more charge carriers on the cold side and thus yield an increase in the thermoelectric voltage.

The Seebeck coefficient (or thermopower) is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across a given material. The Seebeck coefficient has units of volts per degrees kelvin.

\[ S = \frac{\Delta V}{\Delta T} \]  

The Seebeck coefficient, S, depends on a material's temperature, and crystal structure. Typically, metals have small thermopowers because most have half-filled bands, including both electrons and holes. Electrons (negative charges) and holes (positive charges) both contribute to the induced thermoelectric voltage thus tending cancel their contributions to this voltage, resulting in a low net voltage. In contrast, semiconductors can be doped with an excess amount of electrons or holes and therefore can have large positive or negative values of the thermopower depending on the charge of the excess carriers. The sign of the thermopower indicates which charged carriers dominate the electric transport in both metals and semiconductors.

Accurate measurement of the Seebeck coefficient is critical for the performance assessment of thermoelectric materials. High temperature (e.g. greater than 500 C) Seebeck coefficient measurement systems are necessary for efficient and progressive development of thermoelectric materials for waste heat harvesting applications. The history and challenges of Seebeck coefficient measurement have been recently reviewed. See e.g. J. Martin, T. Tritt, and C. Uhler, J. Appl. Phys. 108, 121101 (2010), which is incorporated by reference herein.

In view of the foregoing, there is a need in the art for improved apparatuses and methods for measuring the Seebeck coefficient of thermoelectric materials. There is a particular need for such apparatuses and methods to operate at high temperatures (e.g. above 500 C). Further, there is a need for such apparatuses and methods to be simple, non-destructive, efficient, fast and affordable. There is also a need for such systems and methods to be suitable for bulk material samples in a broad range of physical types and shapes. These and other needs are met by embodiments of the present invention as detailed hereafter.

SUMMARY OF THE INVENTION

A high temperature Seebeck coefficient measurement apparatus and method with various features to minimize typical sources of errors is described. Common sources of temperature and voltage measurement errors which may impact accurate measurement are identified and reduced. Applying the identified principles, a high temperature Seebeck measurement apparatus and method employing a uniaxial, four-point geometry is described which can operate from room temperature up to approximately 850K or even as high as 1300K in some applications. These techniques for non-destructive Seebeck coefficient measurements are simple to operate, and are suitable for bulk samples with a broad range of physical types and shapes.

A typical embodiment of the invention comprises an apparatus for measuring a Seebeck coefficient of a sample, including a first heater assembly having a first bore therethrough exiting at a first substantially perpendicular surface for contacting and producing a first isothermal sample surface, a first thermocouple having a first axis where temperature and voltage are sensed at an end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface, and a second heater assembly having a second bore therethrough exiting at a second substantially perpendicular surface for contacting and producing a second isothermal sample surface on a sample side opposite the first isothermal sample surface, and a second thermocouple having a second axis where temperature and voltage are sensed at an end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface. In some embodiments, the first bore and the second bore are aligned such that the first axis of the first thermocouple and the second axis of the second thermocouple are substantially collinear. Compressive springs may be used to apply force to the sample between the first heater assembly and the second heater assembly.

In some embodiments, the first thermocouple and the second thermocouple may each comprise an electrically insulating cylinder having four bores exiting at an end surface of the cylinder and two thin wires. Each wire is threaded through
two of the four bores and crossed to contact each other at the end surface. Typically, the two thin wires may comprise material combinations X/Y of niobium/chromel, niobium/tungsten, niobium/tungsten-constantan, or gold-iron/chromel, where X is a first wire material disposed on top of a second wire material Y. In addition, the electrically insulating cylinder of each thermocouple may comprise a ceramic, such as mullite.

In further embodiments, the first heater assembly and the second heater assembly may each comprise an insulating ceramic. In addition, the first heater assembly and the second heater assembly may each comprise a plurality of embedded cartridge heaters.

A typical method embodiment of measuring a Seebeck coefficient of a sample the invention comprises disposing a first heater assembly having a first bore therethrough exiting at a first substantially perpendicular surface to contact the sample and produce a first isothermal sample surface, disposing a second heater assembly having a second bore therethrough exiting at a second substantially perpendicular surface to contact the sample and produce a second isothermal sample surface, measuring temperature of the first isothermal sample surface with a first thermocouple having a first axis where temperature and voltage are sensed at an end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface, measuring voltage of the first isothermal sample surface with the first thermocouple, measuring temperature of the second isothermal sample surface with a second thermocouple having a second axis where temperature and voltage are sensed at an end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface, measuring voltage of the second isothermal sample surface with the second thermocouple, and calculating the Seebeck coefficient of the sample from the temperatures and voltages of the first isothermal sample surface and second isothermal sample surface. This method embodiment of the invention may be further modified consistent with the apparatus embodiments described herein.

Another typical embodiment of the invention may comprise a first heater assembly means for contacting and producing a first isothermal sample surface, the first heater means having a first bore therethrough exiting at a first substantially perpendicular surface, a first thermocouple means for measuring temperature and voltage, the first thermocouple means having a first axis where temperature and voltage are sensed at an end of the first axis, the first thermocouple means disposed in the first bore of the first heater assembly means to contact the first isothermal sample surface, a second heater assembly means for contacting and producing a second isothermal sample surface on a sample side opposite the first isothermal sample surface, the second heater assembly means having a second bore therethrough exiting at a second substantially perpendicular surface, and a second thermocouple means for measuring temperature and voltage, the second thermocouple means having a second axis where temperature and voltage are sensed at an end of the second axis and the second thermocouple means disposed in the second bore of the second heater assembly means to contact the second isothermal sample surface. This embodiment of the invention may be further modified consistent with the apparatus or method embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIG. 1 is a schematic diagram of ideal measurement geometry for the Seebeck coefficient, with thermocouples making small point contacts;

FIG. 2A is a cross-section view of an example two-point geometry where thermocouples are embedded in heater and heat sink blocks for measurement of the Seebeck coefficient;

FIG. 2B is a cross-section view of an example off-axis four-point geometry where thermocouples contact the side of the sample for measurement of the Seebeck coefficient;

FIG. 2C is a cross-section view of an example uniaxial four-point geometry where thermocouples contact ends of the sample through heater and heat sink blocks for measurement of the Seebeck coefficient;

FIG. 3A shows an example of a Seebeck voltage and associated temperature measurement spatial dislocation;

FIG. 3B shows an exemplary crossed-wire geometry may be applied to minimize Seebeck voltage and associated temperature measurement spatial dislocation;

FIG. 4A is a schematic drawing of an exemplary uniaxial four-point Seebeck coefficient measurement instrument;

FIG. 4B is a three-dimensional drawing of the exemplary uniaxial four-point Seebeck coefficient measurement instrument;

FIG. 4C is a detailed three-dimensional drawing of the thermocouple compression assembly of the upper plate of the exemplary uniaxial four-point Seebeck coefficient measurement instrument;

FIG. 4D is a schematic diagram of an exemplary measurement apparatus embodiment of the invention to illustrate some of the fundamental features included in the detailed apparatus of FIGS. 4A-4C;

FIG. 5 shows plots of exemplary test results of the top and bottom temperature of the sample applying different temperature gradients, and the resulting derived Seebeck coefficient as the slope of the voltage response; and

FIG. 6 is a flowchart of an exemplary method of measuring the Seebeck coefficient according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

1. Overview

FIG. 1 shows the ideal measurement geometry for the Seebeck coefficient where two probes 106, 108 make point contacts with the sample material 100 at precise locations across a temperature gradient between a hot side 102 and a cold side 104 of the sample material 100. In principle, measurement of the Seebeck coefficient in bulk materials is relatively simple. One needs to know the temperature gradient between two locations on a sample, and the voltage across the two points. The probes 106, 108 serve as both the thermocouples as well as the voltage measurement leads, across which the temperature gradient and voltage present are measured. (It should be noted that for every example measurement system described herein, thermocouples also serve as the voltage measurement leads unless otherwise stated.) For an ideal measurement of the Seebeck coefficient, certain assumptions are applied. First, the system is assumed to be in steady state during the measurement of the temperature and voltage, and that both measurements occur simultaneously. In addition, it is also assumed that the voltage response to the temperature gradient is linear and that the measurement of the temperature and voltage occur at the same point on the sample for each probe.

It should be noted that throughout this description a temperature gradient across a material may be established by two
elements, one having a hotter temperature than the other. These elements may be described as either a heater or a cooler depending upon their temperatures relative to the ambient temperature. However, the term, “heater,” will be used generically throughout this description to mean both the hotter and the colder element used in a system. Measurement of the Seebeck coefficient only concerns their temperatures relative to each other; their temperatures relative to the ambient temperature is not a factor.

However, in a real instrument, non-negligible errors often result due to the inability to achieve these ideal conditions. For example, temperature and voltage measurements often occur at different times in practice. In addition, the voltage response to the temperature gradient is often not linear in practice due to insufficient signal or non-zero voltage at \( \Delta T = 0 \). Furthermore, during high temperature measurements, there is often a noticeable voltage offset that results in significant inaccuracies arising from simple \( \Delta V/\Delta T \) measurement. The origin of this voltage offset may be unclear, but it has been found to increase with temperature and can become particularly significant at temperatures greater than 300°C. Finally, true co-location of the measurement of the temperature and voltage is almost never attained, as there is always some distance between the temperature and voltage measurement locations due to the finite size of the temperature sensor. The smallest point source temperature sensor used in Seebeck measurement is a thermocouple. However, in a thermocouple junction, the temperature where the wires meet is not necessarily the same as the sample temperature associated with the voltage measurement.

Having identified the foregoing sources of Seebeck coefficient measurement error, embodiments of the present invention are directed to minimizing these effects in order to obtain more accurate measurements of the Seebeck coefficient.

2. Seebeck Coefficient Measurement Geometries

Since any real instrument setup will deviate from ideal measurement conditions, it is important to consider which geometric design and measurement techniques provide minimum errors. Currently, there are two dominant measurement geometries known in the art, a two-point geometry where thermocouples are embedded in heater and heat sink blocks and an off-axis four-point geometry where thermocouples contact the side of the sample. Two-point geometry refers to the co-location of the thermocouples and the heating and heat sink blocks; heating/cooling and measurement occurs between two points. Four-point geometry refers to a separation between the thermocouples and the heating and heat sink blocks; heating and heat sinks are between two points and measurement occurs between two different points. Off-axis/uni-axial refers to the axes of the thermocouples used to measure the Seebeck coefficient, i.e., whether they are along different axes (off-axis) or along a common axis (uni-axial). This terminology is applicable to thermocouples configured with at least a portion having a slender geometry with an identifiable axis where measurement is sensed at one end of the axis. When force is applied to a thermocouple (e.g., by a spring), the direction of the force can define the direction of the axis and the position of the thermocouple defines the position of the axis.

FIG. 2A is a cross-section view of an example two-point geometry where thermocouples 200A, 200B are embedded in heater and heat sink blocks 202A, 202B for measurement of the Seebeck coefficient. In this geometry, a bulk sample 204 is placed between two metal blocks 202A, 202B, which act as a heater source and a sink, respectively, to establish the thermal gradient. In this case, the thermocouples 200A, 200B are embedded in these blocks 202A, 202B. In this example two-point geometry shown in FIG. 2A, the thermocouple and voltage sensors are embedded into the blocks rather than directly contacting the sample. This setup gives the advantage of avoiding possible chemical reactions between the sample and the thermocouple materials (which will be discussed later) and can accommodate a wide range of sample geometries. However, this system inherently has thermal and electrical contact resistance in these metal blocks themselves, as well as across the interfaces between the sample and the metal blocks. In particular, the thermal contact resistances are often large enough to lead to inaccuracies in the temperature measurement.

FIG. 2B is a cross-section view of an example off-axis four-point geometry where thermocouples 210A, 210B contact the side of the sample 214 (i.e., “off” the central axis of the sample) for measurement of the Seebeck coefficient. In this case, a long bar sample 214 is sandwiched between a heater 212A and a heat sink 212B. In this configuration the two thermocouples 210A, 210B contact the sample 214 at two locations along the temperature gradient. This geometry is used by the ZEM line of instruments (Ulvac-Riko Inc., Japan). See http://www.ulvac-riko.co.jp/English/B-9en.html, which is incorporated by reference herein.

It is known that four-point electrical resistance measurements are an improvement on the two-point technique for materials with low electrical impedance. In a similar manner, a four-point thermal design can reduce the effect of thermal contact resistance. Such a design is shown in FIG. 2B, where the key difference from the two-point geometry of FIG. 2A is the placement of the thermocouples along the side of the sample. While this important modification eliminates the thermal contact resistance between the sample and the heat source/sink, several critical issues remain.

Off-axis four-point geometry measurement (e.g. as in the example of FIG. 2B) still presents potential issues which undercut accuracy of the Seebeck coefficient measurement. The first issue typically arises at higher temperatures, where the thermal conductance of the thermocouples can draw heat away from the sample (the so-called “cold-finger effect”) leading to a temperature difference across the thermocouple bead. This effect can result in a voltage and temperature measurement dislocation, where with the separate measurements are made at different locations having different temperatures. (This effect is described in further detail hereafter regarding FIG. 3A.) Second, lateral spring loading of the thermocouples into the sample is required to ensure good thermal contact between the thermocouples and the sample surface. At high temperatures, plastic deformation often occurs in softer samples and this can lead to poor thermal contact. On the other hand, side loading can lead to sample fracture or breakage with brittle samples. Furthermore, if low spring forces are used in an attempt to accommodate the side loading issues, high contact resistance between the thermocouple and the sample can result.

An additional issue of off-axis four-point geometry measurement is that it requires that samples be in an elongated geometry to develop a low \( d\Delta T/dz \) across the thermocouple-sample junctions. (The elongated sample geometry is illustrated between the samples of FIGS. 2A and 2B where the sample 214 has a much small width compared to its length than the other sample 204.) This is necessary since there is uncertainty in the temperature reading if the junction contacts a sample surface that has a temperature gradient. Shaping the sample into an elongated geometry can be difficult for some materials, since the better thermoelectric materials are often brittle. Thus, samples can be damaged during cutting. Furthermore, this geometry is unsuitable for flash diffusivity
provides voltage signals measureable with a modern voltage
sensitive measurement and thermal diffusion.

A round pellet with a diameter of 10 to 25 mm and thickness of
0.5 to 1 mm is disposed through the heater element 222A. In this
example setup, a combination of niobium and chromium may
be used. However, some minor drawbacks may be that these
materials are rather reactive to heavy metals such as Pb, Te, Ag, Bi and Sb.

As shown in FIG. 2C, the cylindrical heater element 222A,
which may be constructed from a piece of machinable boron
nitride, has a bore through the center. A thermocouple 220A
shielded with a four-bore ceramic cylinder, which has a
slightly smaller diameter compared to the diameter of the
bores, is disposed through the heater element 222A. In this
example design, the thermocouple probe tip is heat-sunk to
the heater, thereby reducing cold-finger effects. This
configuration is in contrast to the off-axis design of FIG. 2B,
where the cold finger effect is exacerbated by the thermo-
couple-sample contact resistance and the temperature differ-
cence between the sample and ambient temperature.

Regarding thermocouple junction contacts, FIG. 2C shows
how thermocouple junctions contact the uniform temperature
regions of opposite sample surfaces created by a heater and
heat sink blocks making an intimate contact with the sample.
In each geometry shown in FIGS. 2A-2C, the heaters/heat
sinks establish a temperature gradient along the principle axis
of the samples. The off-axis geometry of FIG. 2B only allows
the finite size thermocouple bead to contact the surface with
a temperature gradient. Only the geometry in FIG. 2C allows
the thermocouple junction to make contact with an isothermal
surface.

An additional benefit with the FIG. 2C geometry of the
heaters/heat sinks and thermocouples is that, like the FIG. 2A
geometry, a wide range of sample shapes and sizes can be
accommodated, with only requirement of having two flat
sides substantially parallel to each other. In a typical bulk
sample fabrication technique (such as hot press method), a
round pellet with a diameter of 10 to 25 mm and thickness of
1 to 2 mm is easily created. This example bulk sample size is
convenient because it is in a sample dimension range also
required for the hall effect measurement and thermal diffu-
sivity measurement (e.g. using the flash method), other
properties typically measured for thermoelectric materials.
Further, since the heaters allows exertion of the full ΔT across
the sample, even a pellet with thickness as thin as nearly 0.5 mm
provides voltage signals measurable with a modern voltage
meter.

Finally, the geometry of FIG. 2C also allows all the compres-
sive forces by springs applied along a single principle
axis to make good thermo-mechanical contacts with the
sample. As will be described in hereafter, the springs attached
on the heater assembly may be designed to exert vertical
forces onto the sample for good contact between the heaters
and the sample surfaces. The compression springs on the back
end of thermocouple junctions, which are independent from the heater
springs, can apply strong vertical force to the thermocouple
junctions against the sample surface. This design is attractive
for both brittle and soft materials because the stresses are
compressive and no tensile stresses result which might propa-
gate cracks in the sample.

4. EXEMPLARY THERMOCOUPLE DESIGN

Here, some features on the thermocouple design incorpo-
rated to improve temperature and voltage measurements are
addressed. In a typical temperature measurement in high tem-
perature environment, thermocouple types such as S or R,
ones that contain platinum wires may be used. In one example
setup, however, a thermocouple type which sustains up to
approximately 925 °C may be used, simply constructed from
niobium and chromel wires. There are at least a couple of
reasons for this choice.

First, as previously mentioned, a chemical reaction
between the thermocouple and the sample may occur at their
contact point and adversely affect the Seebeck slope and
voltage offset. In order to minimize this effect, thermocouples
having minimal reactivity with the sample should be chosen.
Platinum thermocouples, while resistant to oxidation, are
rather reactive to heavy metals such as Pb, Te, Ag, Bi and Sh.
Even nickel has some reactivity with certain thermoelectric
elements at high temperatures. Therefore, thermocouple
wires that are inert to heavy metals may be preferable.

Another consideration in the selection of a thermocouple
type due to the fact that Seebeck coefficient measurement
systems typically use one of the thermocouple wires for the
voltage measurement. It is noted that the Seebeck effect also
occurs in the thermocouple wires, and the voltage reading is
a summation of the Seebeck voltages from two wires in
addition to the Seebeck voltage from the sample. Although
voltages from the wires are opposite in polarity, they do not
cancel each other because the magnitudes are not the same:
the temperature differences between the contact points and
the cold junction of the instruments are different. This
residual voltage can falsely increase or decrease the measured
Seebeck voltage, depending on the material charge carrier
type.

The error induced by this factor is very apparent when
measuring low Seebeck coefficient materials with high ther-
mal conductivity (e.g. tungsten). To reduce this effect, a near-
zero Seebeck coefficient metal, such as copper or niobium
should be used for the voltage probe. This probe is also used
as one leg of the thermocouple when combined with a high
Seebeck coefficient metal. While the resulting thermocouple
supplies only half the voltage of traditional thermocouples,
measurement of this reduced signal is well within the capa-
bilities of modern electronics.

For high temperatures, tungsten and niobium have been
found to be preferable due to their low reactivity. In one
example setup, a combination of niobium and chromium may
be used. However, some minor drawbacks may be that these
materials must be used in an oxygen free environment and are
poor thermocouples for near-room temperature operation.
However, embodiments of the invention may be implemented
in vacuum or inert atmospheric environments (e.g. Argon,
Helium, or Nitrogen). An oxygen environment may be used
with proper selection of thermocouple materials (e.g. plat-

7
8
In order to provide an additional barrier against possible chemical reaction, a thin, flexible, graphite sheet (e.g. Grafoil from GrafTech International Inc, Ohio) may be used between the interface of the sample and thermocouple. With high thermal conductivity (approximately 5 W/mK at room temperature) and low electrical resistivity (approximately 1.15 mΩm at room temperature), these sheets also provide good thermal contact between the sample and the heating blocks while not interfering with the voltage measurements.

FIG. 3A shows an example of a Seebeck voltage and associated temperature measurement spatial dislocation. This spatial variation can lead to errors when thermal gradients are present across the thermocouple beads 310, 312, the welded joints of the thermocouple. As shown, measured temperatures, T1 and T2, may be located at the tops of the thermocouple beads 310, 312, whereas the measured voltages, V1 and V2, are located at the base of the beads 310, 312 (at different temperatures). While many instruments measuring Seebeck coefficient utilize thermocouples with welded beads as shown in FIG. 3A, novel “crossed-wire” thermocouples described below offer definite advantages.

FIG. 3B shows an exemplary crossed-wire geometry may be applied to minimize Seebeck voltage and associated temperature measurement spatial dislocation. In one example crossed geometry, two wires 300A, 300B (e.g. one niobium and one chromel) are made to cross threaded down a four-bore ceramic cylinder 302. Each wire 300A (or 300B) is threaded up one bore 304A (or 304C) and across the end surface 308 and back down an opposing bore 304B (or 304D). Here, the contact between the wires 300A, 300B is mechanically not (not welded) and governed only by the geometry of the crossed wires 300A, 300B. To minimize the temperature gradients across the thermocouple junction region, extremely thin (e.g. 0.1 mm diameter) wires 300A, 300B may be used. In contrast, thermocouple beads (e.g. in FIG. 3A) are typically approximately 1 mm in diameter. To further ensure that the junction is nearly isothermal, the ceramic cylinder 302 used to house the wires may be made of low thermal conductivity mullite (e.g. approximately 1.7 mm diameter).

Although such a thin mullite cylinder may be delicate, the element of the assembly that provides a surface for a spring 422A, 422B to contact and apply force to the thermocouple 300A, 300B is a collar clamp 420A, 420B which provides a surface for a spring 422A, 422B to contact and apply force to the thermocouple 300A, 300B. This uniaxial four-point Seebeck coefficient measurement apparatus employs a horizontal mirror plane through the center of the sample 402. The sample 402 is in contact with two boron nitride cylinder heater assemblies 404A, 404B which each have a ring of a plurality of embedded cartridge heaters (e.g., six), installed parallel to the sidewalls of the cylinders. The cartridge heaters are electrically powered and may be controlled with feedback from separate thermocouples 432A, 432B embedded in each heater assembly 404A, 404B. This annular, symmetric heater cartridge placement around the contact area allows uniform distribution of heat to the sample. Boron nitride of the heater assemblies 404A, 404B satisfies the need for an insulating, chemically inert contact and additionally provides high thermal conductivity. However, the heater assemblies may be formed from any other suitable insulating ceramic material such as alumina, “machineable ceramics,” silicon carbide. In addition, some metals may also be used, provided the sample 402 and thermocouples 416A, 416B are electrically insulated from ground (by either electrically insulating these elements from the metal heater block by electrically insulated the metal heater block from the remainder of the apparatus). Thin walled Inconel (Special Metals Corporation Inc., New York) cylinders 406A, 406B are threaded into each heater assembly 404A, 404B and coupled to baseplates 408A, 408B at the upper and lower ends via collar clamps. This adjustable, three-legged geometry ensures good mating between the upper and lower heater assemblies 404A, 404B. The upper and lower baseplates 408A, 408B are aligned through the use of a framework rod 410A-410C at each corner. Compressive force is exerted on the baseplates 408A, 408B, which is carried through the sample 402, from springs 414A, 414C controlled by wing-nuts 412A-412C attached to the framework rods 410A, 410C above the upper baseplate 408A. Together, the elements of the assembly immobilize the sample 402 and achieve superior thermal contact with the heater assemblies 404A, 404B.

For the measurement of the Seebeck coefficient, long (e.g. 20 cm) crossed-wire thermocouples 416A, 416B travel along the central axis of the instrument to the sample 402. The thermocouple wires are contained within four-bore mullite cylinder, 5/6 inch in diameter, as previously described in detail in FIG. 3B. Mullite may be chosen because it has lower thermal conductivity compared to alumina, which is the typical material of choice. From the sample 402, each thermocouple 416A, 416B passes through a boron nitride heater assembly 404A, 404B, a baseplate 406A, 406B and into a thermocouple compression assembly (TCA) 418A, 418B at the upper and lower ends of the apparatus 400.

The purpose of the TCA 418A, 418B is to provide low thermal contact resistance between the sample 402 and the thermocouples 416A, 416B. The TCA 418A, 418B allows forces to be independently applied to the thermocouples 416A, 416B (with even greater pressure) than the springs 414A-414C acting against the heater assemblies. Attached to each thermocouple 416A, 416B is a collar clamp 420A, 420B which provides a surface for a spring 422A, 422B to contact and apply force to the thermocouple 416A, 416B. An adjust-
able plate 424A, 424B in the center of the TCA sets the compression on this spring 422A, 422B. The uppermost assembly 426A, 426B in the TCA provides structural support to the thermocouple 416A, 416B in case of shearing force being inadvertently applied by the operator. When changing samples 402, the spring 422A, 422B within the TCA exerts a force on the collar clamp 420A, 420B and which can drive the thermocouple 416A, 416B tip past the heater assembly 404A, 404B. Such motion exposes the thermocouple 416A, 416B tip, which is mechanically weak and may readily fracture. To avoid this motion, the opposing plate 428A, 428B on the TCA is used to compress the spring 422A, 422B when the sample 402 is replaced. For the purposes of illustration, the upper TCA 418A shows this plate engaged, while the lower TCA 418B shows the plate when the collar clamp is free to move. The measurement assembly 400 may be supported on three legs 430A-430C which are sufficiently long to provide access to the lower TCA 418B.

For PID temperature control, the boron nitride cylinders of the heater assemblies 404A, 404B may have additional thermocouples 432A, 432B embedded in them. These thermocouples 432A, 432B are not used to measure the Seebeck coefficient, but are used instead for temperature control of heater assemblies 404A, 404B.

FIG. 41D is a schematic diagram of an exemplary measurement apparatus 450 embodiment of the invention to illustrate some of the fundamental features included in the detailed apparatus 400 of FIGS. 4A-4C. The elements of this apparatus 450 and those of apparatus 400 are interchangeable and functionally consistent. The sample 402 is disposed between two heater assemblies 404A, 404B. Each heater assembly 404A, 404B may comprise a cylinder element, c.g. of boron nitride. A plurality of cartridge heaters 452A, 452B are embedded in each of the heater assemblies 404A, 404B. Although any suitable number of cartridge heaters or other suitable heating device may be used, in one example six cartridge heaters may be embedded in each heater assembly 404A, 404B, one in a radial pattern. Pressure between the heater assemblies 404A, 404B and the sample 402 is applied and controlled by compression springs 414A-414C of the support structure (as described regarding FIGS. 4A-4C). The heater assemblies 404A, 404B are operated to establish isothermal at opposite surfaces 454A, 454B of the sample 402. Separate thermocouples 432A, 432B may be embedded in each of the heater assemblies 404A, 404B in order to monitor their temperatures.

Long cylindrical thermocouples 416A, 416B are disposed within bores through each of the heater assemblies 404A, 404B. The heater assemblies 404A, 404B are aligned such that axes of the thermocouples 416A, 416B are substantially collinear. Each thermocouple comprises an electrically insulating cylinder having four bores exiting at an end surface 456A, 456B of the cylinder. Two thin wires are threaded through two of the four bores and cross to contact each other at the end surface 456A, 456B. See FIG. 3B. Pressure between the thermocouples 416A, 416B and the sample 402 is applied and controlled by other compression springs 422A, 422B of the supporting structure (as described regarding FIGS. 4A-4C).

FIG. 5 shows plots of exemplary test results of the top and bottom temperature of the sample applying different temperature gradients, and the resulting derived Seebeck coefficient as the slope of the voltage response. These plots show temperature oscillations in an example high temperature run. The temperatures shown in the top two plots are taken from the Seebeck measurement thermocouples 416A, 416B. For measurements at each temperature, the temperature gradient is oscillated using the heater assemblies 404A, 404B about a fixed average temperature, as shown in FIG. 5B. The resulting voltage response to the temperature gradient is shown in FIG. 5C, and reveals a substantially linear relationship with the slope as the value of Seebeck coefficient.

Several benefits are worth noting regarding this particular exemplary Seebeck coefficient measurement apparatus 400 design. The apparatus portion above an imaginary horizontal mirror plane through the center of the sample, including the thermocouple compression assembly (TCA), is assembled in one piece, and it can be manually moved vertically when mounting a sample. Its vertical range of movement is guided by framework rods 410A-410C that pass through three holes located at the three corners of the triangular upper baseplate 408A. Since these holes are larger than the diameter of the framework rods 410A-410C, there is allowance for the upper plate assembly (all the elements comprising the heater assemblies 404A, 404B) to be positioned against a sample surface having some angular deviation from horizontal. Thus, the flexibility of the design allows better contacts between the sample 402 and the heater assemblies 404A, 404B when the sample surfaces are not exactly parallel.

In addition, all springs are located distant from the sample heating area, so that they do not lose compression due to heating. This uniaxial design also affords some clearance around the sample heating area. Accordingly, a cylindrical heat shield 460 or clam-shell furnace may be disposed around the sample heating area. This heat shield 460 can help ensure uniform heating near the sample area.

6. Exemplary Method of Measuring the Seebeck Coefficient

FIG. 6 is a flowchart of an exemplary method 600 of measuring the Seebeck coefficient. The method 600 includes an operation 602 of disposing a first heater assembly 404 having a first bore therethrough exiting at a first substantially perpendicular surface to contact the sample and produce a first isothermal sample surface. In operation 604 a second heater assembly 404 having a second bore therethrough exiting at a second substantially perpendicular surface is disposed to contact the sample and produce a second isothermal sample surface on a sample side opposite the first isothermal sample surface. In operation 606 temperature of the first isothermal sample surface is measured with a first thermocouple having a first axis where temperature and voltage are sensed at the end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface. In operation 608, voltage of the first isothermal sample surface is measured with the first thermocouple. In operation 610, temperature of the second isothermal sample surface is measured with the second thermocouple having a second axis where temperature and voltage are sensed at the end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface. In operation 612, voltage of the second isothermal sample surface is measured with the second thermocouple. Finally in operation 614, the Seebeck coefficient of the sample is calculated from the temperatures and voltages of the first isothermal sample surface and second isothermal sample surface.

This method 600 may be altered consistent with the various apparatus embodiments previously described. It is important to note that the steps may be performed in any suitable order. In addition, although simultaneous measurement of temperature and voltage is ideal, it is not required and timing of the measurements may be manipulated to improve results as discussed hereafter.
Beyond the example measurement apparatus structures previously described, the measurement process can be altered to further improve accuracy in determining steady-state measurements of the Seebeck coefficient. As previously discussed, ideally all steady state measurements should occur simultaneously. In practice, measurements of temperature and voltage are often conducted sequentially, however. A first-order correction to thermal drift may be achieved by using the delta method, where measurements are symmetric with time. See V.H. Weiss, *Z. Naturforsch. B*, 11a, 131 (1965), which is incorporated by reference herein. For example, measurements taken in the order $T_1, T_2, V, T_3, T_4$ at equally spaced intervals in time to account for linear drift when $T_1 = (T_2 + T_3)/2$ and $T_4 = (T_1 + T_3)/2$. This technique of taking temperature and voltage measurements symmetric with time may be applied directly to the method of measuring the Seebeck coefficient as will be understood by those skilled in the art.

The multiple gradient method measures the voltage difference for various $\Delta T$s (both positive and negative) with the same average temperature of the sample. Non-linear behavior using the multiple gradient technique can be indicative of a poor signal-to-noise ratio, requiring larger $\Delta T$. A $\Delta T$ of 3% of the absolute sample temperature is often appropriate, for example.

This concludes the description including the preferred embodiments of the present invention. The foregoing description including the preferred embodiment of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible within the scope of the present invention may be devised without departing from the inventive concept as set forth in the following claims.

What is claimed is:

1. An apparatus for measuring a Seebeck coefficient of a sample, comprising:
   a first heater assembly having a first bore therethrough exiting at a first substantially perpendicular surface for contacting and producing a first isothermal sample surface;
   a first thermocouple having a first axis of a first slender geometry where temperature and voltage are sensed at an end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface;
   a second heater assembly having a second bore therethrough exiting at a second substantially perpendicular surface for contacting and producing a second isothermal sample surface; and
   a second thermocouple having a second axis of a second slender geometry where temperature and voltage are sensed at an end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface.

2. The apparatus of claim 1, wherein the first bore and the second bore are aligned such that the first axis of the first thermocouple and the second axis of the second thermocouple are substantially collinear.

3. The apparatus of claim 1, wherein the first thermocouple and the second thermocouple each comprise an electrically insulating cylinder having four bores exiting at an end surface of the cylinder and two thin wires, each wire threaded through two of the four bores and crossing to contact each other at the end surface.

4. The apparatus of claim 3, wherein the two thin wires comprise material combinations X/Y of niobium/chromel, niobium/tungsten, niobium/tungsten-rhenium, copper/constantan, or gold-iron/chromel, where X is a first wire material disposed on top of a second wire material Y.

5. The apparatus of claim 3, wherein the electrically insulating cylinder comprises a ceramic.

6. The apparatus of claim 5, wherein the ceramic comprises mullite.

7. The apparatus of claim 1, wherein the first heater assembly and the second heater assembly each comprise an insulating ceramic.

8. The apparatus of claim 7, wherein the first heater assembly and the second heater assembly each comprise a plurality of embedded cartridge heaters.

9. The apparatus of claim 1, further comprising compressive springs to apply force to the sample between the first heater assembly and the second heater assembly.

10. A method of measuring a Seebeck coefficient of a sample comprising the steps of:
   disposing a first heater assembly having a first bore therethrough exiting at a first substantially perpendicular surface to contact the sample and produce a first isothermal sample surface;
   disposing a second heater assembly having a second bore therethrough exiting at a second substantially perpendicular surface to contact the sample and produce a second isothermal sample surface on a sample side opposite the first isothermal sample surface;
   measuring temperature of the first isothermal sample surface with a first thermocouple having a first axis of a second slender geometry where temperature and voltage are sensed at an end of the first axis, the first thermocouple disposed in the first bore of the first heater assembly to contact the first isothermal sample surface;
   measuring temperature of the first isothermal sample surface with the first thermocouple; measuring temperature of the second isothermal sample surface with a second thermocouple having a second axis of a second slender geometry where temperature and voltage are sensed at an end of the second axis, the second thermocouple disposed in the second bore of the second heater assembly to contact the second isothermal sample surface;
   measuring voltage of the second isothermal sample surface with the second thermocouple; and calculating the Seebeck coefficient of the sample from the temperatures and voltages of the first isothermal sample surface and second isothermal sample surface.

11. The method of claim 10, wherein the Seebeck coefficient is calculated from temperature and voltage measurements taken symmetric with time.

12. The method of claim 10, further comprising aligning the first bore and the second bore such that the first axis of the first thermocouple and the second axis of the second thermocouple are substantially collinear.

13. The method of claim 10, wherein the first thermocouple and the second thermocouple each comprise an electrically insulating cylinder having four bores exiting at an end surface of the cylinder and two thin wires, each wire threaded through two of the four bores and crossing to contact each other at the end surface.

14. The method of claim 13, wherein the two thin wires comprise material combinations X/Y of niobium/chromel, niobium/tungsten, niobium/tungsten-rhenium, copper/constantan, or gold-iron/chromel, where X is a first wire material disposed on top of a second wire material Y.
stantan, or gold-iron/chromel, where X is a first wire material disposed on top of a second wire material Y.

15. The method of claim 13, wherein the electrically insulating cylinder comprises an insulating ceramic.

16. The method of claim 15, wherein the ceramic comprises mullite.

17. The method of claim 10, wherein the first heater assembly and the second heater assembly each comprise boron nitride.

18. The method of claim 10, wherein the first heater assembly and the second heater assembly each comprise a plurality of embedded cartridge heaters.

19. The method of claim 10, further comprising compressive springs to apply force to the sample between the first heater assembly and the second heater assembly.

20. An apparatus, comprising:

- a first heater assembly means for contacting and producing a first isothermal sample surface, the first heater means having a first bore therethrough exiting at a first substantially perpendicular surface;
- a first thermocouple means for measuring temperature and voltage, the first thermocouple means having a first axis of a second slender geometry where temperature and voltage are sensed at an end of the first axis, the first thermocouple means disposed in the first bore of the first heater assembly means to contact the first isothermal sample surface; and
- a second heater assembly means for contacting and producing a second isothermal sample surface on a sample side opposite the first isothermal sample surface, the second heater assembly means having a second bore therethrough exiting at a second substantially perpendicular surface; and
- a second thermocouple means for measuring temperature and voltage, the second thermocouple means having a second axis of a second slender geometry where temperature and voltage are sensed at an end of the second axis and the second thermocouple means disposed in the second bore of the second heater assembly means to contact the second isothermal sample surface.

21. The apparatus of claim 20, wherein the first thermocouple means and the second thermocouple means each comprise an electrically insulating cylinder having four bores exiting at an end surface of the cylinder and two thin wires, each wire threaded through two of the four bores and crossing to contact each other at the end surface.