A high temperature thin film strain gage sensor capable of functioning at temperatures above 1400°C. The sensor contains a substrate, a nanocomposite film comprised of an indium tin oxide alloy, zinc oxide doped with alumina or other oxide semiconductor and a refractory metal selected from the group consisting of Pt, Pd, Rh, Ni, W, Ir, NiCrAlY and NiCoCrAlY deposited onto the substrate to form an active strain element. The strain element being responsive to an applied force.

11 Claims, 6 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
Cycle —®— ITO sputtered in Ar 9 N 1.5 O 0.3 mTorr

Temperature / °C

Resistance / Ω

0 200 400 600 800 1000 1200

1000 1200

FIG. 1

Refractory Metal Target

ITO Target

Argon Plasma

Combinatorial “strain gage” libraries

FIG. 2
Selection of refractory metal candidates

Co-sputtered "libraries"

TCR measurement

Strain sensor testing

Chemical analysis

Plasma spraying of candidate material

Nanocomposite strain gage

FIG. 3
FIG. 4

FIG. 5
Strain Test @800°C

FIG. 6

Secondary Electron Image
Backscattered Electron Image

FIG. 7
<table>
<thead>
<tr>
<th>Phase</th>
<th>Area Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52.04%</td>
</tr>
<tr>
<td>2</td>
<td>47.96%</td>
</tr>
</tbody>
</table>

**FIG. 8**

**FIG. 9**
LOW TCR NANOCOMPOSITE STRAIN GAGES

PRIORITY INFORMATION

This application claims priority to U.S. Provisional Patent Application No. 60/942,017, filed on Jun. 5, 2007, all of which is incorporated herein in its entirety.

GOVERNMENT SPONSORSHIP

This invention was made with government support under Grant No. NNC05GA67G awarded by the National Aeronautic and Space Administration (NASA). The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Ceramic strain gages are being developed to monitor the structural integrity of gas turbine engine components employed in aerospace propulsion and power generation systems. The hot sections of these engines are exposed to gas temperatures in excess of 1500° C. Temperature gradients from the turbine blade tip to the root of the blade can be as large as 450° C. Thus, strain measurement under these conditions using resistance strain gages can lead to considerable error due to apparent strain effects, including thermal expansion coefficient mismatch between the gage and substrate as well as the temperature coefficient of resistance or TCR. Therefore, apparent strain effects are particularly troublesome when the active strain gage elements have an inherently large temperature coefficient of resistance. Apparent strain effects in resistance strain gages can be mitigated by employing strain gages that have a similar thermal expansion to the substrate and a smaller temperature coefficient of resistance, but the choices are much more limited when going to higher temperatures, since the piezoresistive response and chemical and electrical stability become more important under these conditions. However, given that the materials comprising high temperature strain gage element such as indium tin oxide (ITO), have an inherently large temperature coefficient of resistance (See FIG. 1), the choices for temperature compensation are limited to placing resistors or other gage elements in series with the active strain element as taught by O. J. Gregory and Q. Luo. Sensors and Actuators A: Physical Sensors, vol. 88, pp. 234-240 (2001), since most metals typically exhibit positive TCR’s while most semiconductors exhibit negative TCR’s, or using signal conditioning protocols that subtract out the contribution of thermal strain from the total strain to yield the mechanical strain; i.e. if the TCR is well characterized, this portion of the signal can be subtracted from total signal to give an approximate measurement due to mechanical loading.

SUMMARY OF THE INVENTION

A high temperature thin film strain gage sensor capable of functioning at temperatures above 1200° C. The sensor includes a substrate, a nanocomposite film comprised of indium tin oxide alloy, zinc oxide doped with alumina or other oxide semiconductor and a refractory metal such as Pt, Pd, Rh, Ni, W, Ir, NiCrAlY and NiCoCrAlY deposited onto the substrate to form an active strain element. The strain element is responsive to an applied force.

The ITO alloy comprises about 90% weight In2O3 and about 10% weight SnO2 wherein the weights being based on the total weight of the ITO alloy.

These and other features and objectives of the present invention will now be described in greater detail with reference to the accompanying drawings, wherein:

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a graph of the temperature coefficient of resistance of an indium tin oxide strain gage as a function of thermal cycling;

FIG. 2 is a graphic showing an ITO/Pt combinatorial “strain gage” libraries prepared by co-sputtering onto alumina substrates placed in between ITO and Pt or other refractory metal sputtering targets;

FIG. 3 is a graphic protocol used for rapid screening of low TCR strain gage libraries developed from combinatorial materials synthesis;

FIG. 4 is a graph of electrical resistance of several ITO-Pt nanocomposite libraries as a function of temperature;

FIG. 5 is a graph of piezoresistive response of an ITO-Pt nanocomposite strain gage at 800° C. (e=250µe, G=26.0);

FIG. 6 is a graph of piezoresistive response of an ITO-Pt nanocomposite strain gage at 800° C. (e=59 µm/m, G=17.1);

FIG. 7 is a SEM micrograph of an ITO-Pt nanocomposite strain gage with nominal composition of 88% Pt and 12% ITO;

FIG. 8 is an area fraction of ITO and Pt in the nanocomposite;

FIG. 9 is a graph of drift rate of an ITO-Pt nanocomposite strain gage at 800° C.;

FIG. 10 is a SEM micrograph of an ITO-Pt sensor (#4-2); and

FIG. 11 is an EDS spectrum of an ITO-Pt sensor (#4-2).

DESCRIPTION OF THE INVENTION

By combining refractory metals and oxide semiconductors in a single strain gage element (refractory metals that exhibit a positive TCR and semiconductors that exhibit a negative TCR) a TCR approaching zero over an extended temperature range of interest would be feasible. Ceramic thin film strain gages based on indium-tin-oxide (ITO) and refractory metal (Pt, Pd, Rh, Ni, W, Ir and NiCoCrAlY) nanocomposites were prepared in an attempt to form composites with a very low TCR in a single strain element without compromising the piezoresistive response of the strain gage. Nanocomposite sensor elements comprised of a large number of ITO/Pt combinatorial libraries were prepared by reactive co-sputtering onto alumina substrates placed in between ITO and Pt or other refractory metal sputtering targets as shown in FIG. 2. TCR measurements of the nanocomposite sensors were made by thermally cycling the strain gages from room temperature to 1000° C. and the piezoresistive response was measured at strain levels up to 1000µe from room temperature to 1200° C. There are no standards for strain gages operating over 900 C even though there are ASTM standards for strain gage calibration and application to components in general, these are usually restricted to room temperature or slightly above room temperature. The chemical composition of the most promising combinatorial sensor libraries was analyzed by EDS/SEM. The protocol used for rapid screening of the low TCR strain gage libraries developed from combinatorial materials synthesis is shown in FIG. 3.

Preliminary results indicate that a near zero TCR could be achieved for a non optimized nanocomposite strain gage containing less than 10% ITO. Even though EDS revealed that the bulk of the nanocomposite strain sensor was platinum, the gage factor remained relatively large (~26.0) and exhibited a...
very low drift rate (0.018%/hr). Based on these results, other
combinatorial libraries employing ITO/refractory metal
nanocomposites including ITO/Pd, ITO/Ni, ITO/
NiCoCrAlY, ITO/W and ITO/Ir were considered for high
temperature strain gage applications. The TCR's of thin film
refractory metals and corresponding ITO/metal nanocomposites
based on these thin films are summarized in Table 3.

Ceramic strain gages based on reactively sputtered indium
tin oxide (ITO) have been considered for a number of applica-
tions where strain measurements are required at elevated
temperature since they exhibit excellent oxidation resistance
and high temperature electrical stability. Dynamic strain
gages based on indium tin oxide have been demonstrated at
temperatures in excess of 1200° C. However, static strain
measurements have been limited by large apparent strain
effects due to the large, negative temperature coefficient of
resistance (TCR) that is associated with ITO (See FIG. 1).
Large TCR's typically require the implementation of elabo-
rate temperature compensation schemes into the measure-
ment protocols. The large apparent strain effects associated
with ITO can be mitigated by adding compensating sensor
materials to cancel these large apparent strain effects in a
single low TCR composite material. Since refractory metals
typically exhibit a large positive TCR and semiconductors
exhibit a large negative TCR, the combination of these in a
single material at very small length scales could produce
sensor elements with minimal apparent strain. The nanocom-
posite thin film strain gages based on ITO and refractory
metals were prepared in such a way that the strain gage
elements were compensated at very small length scales. The
large surface area to volume ratio along with the optimal
phase distribution can produce metallic phases with dimen-
sions smaller than the mean free path for electron scattering
and thus, electron scattering will occur largely at grain bound-
aries. As a result, the electrical resistivity and TCR will be
greatly affected by the distribution of phases in the nano-
composite, since electrical conduction in ITO is also governed
by grain boundary transport as well. Nanocomposite strain ele-
ments comprised of ITO(Pt, Pd, W, NiCoCrAlY, Ni and Ir)
combinatorial libraries were prepared by co-sputtering from
ITO and refractory metal targets to reduce the TCR over the
temperature range of interest (500-1100° C.).

Static strain measurement using resistance strain gages is
difficult because resistance is not only a function of strain, but
also functions of temperature and time, i.e., R = R(e, t, T). To
a first approximation, the relative change in resistance of a
strain gage is:

\[
\frac{\Delta R}{R} = \frac{1}{\Delta e} \frac{\partial R}{\partial e} |_{T, e} \Delta e + \frac{1}{\Delta T} \frac{\partial R}{\partial T} |_{e, T} \Delta T + \frac{1}{\Delta t} \frac{\partial R}{\partial t} |_{e, T} \Delta t
\]

(1)

where the first term, gage factor, is a measure of the piezo-
resistive response or sensitivity of the gage. The second term is
a measure of the 'apparent strain' and is due to the thermal
expansion mismatch between the gage and substrate and the
temperature coefficient of resistance of the gage material. The
third term in equation (1), drift rate (DR), reflects the elec-
trical stability. These three factors represent the performance
metrics of a strain gage and can be individually calculated by
the equations below:

\[
G = \frac{\Delta R}{R} \frac{1}{\Delta e}
\]

(2)

\[
TCR = \frac{\Delta R}{R} \frac{1}{\Delta T}
\]

(3)

\[
DR = \frac{\Delta R}{R} \frac{1}{\Delta t}
\]

(4)

where R is the initial resistance, \(\Delta R\) is the change in resis-
tance, \(\Delta t\) is the applied strain, \(\Delta T\) is the change in temperature
and \(\Delta t\) is the length of time.

To measure the resistance change due to the mechanical
strain alone, the effects that cause the resistance to change
with temperature have to be eliminated. In previous work, a
self-compensated strain gage was fabricated using thin film
platinum resistors placed in series with an active ITO strain
element and a near zero TCR was achieved by this method
from room temperature to 1400° C. In present work, low TCR
nanocomposite strain gages were fabricated by co-sputtering
ITO and platinum. Hence the ITO phase with a characteristic
size on the order of nanometers was embedded in a metal
matrix using non-equilibrium physical vapor deposition pro-
cesses.

Nanocomposites comprised of ITO-Ni, ITO-Pt, ITO-Pt,
ITO-NiCoCrAlY, ITO-W and ITO-Ir were evaluated and
ITO-Pt was the most promising combination investigated.
The TCR's for several ITO-Pt combinations are shown in
FIG. 4. Here, the samples were identified according to their
positions relative to the two sputtering targets, e.g., the larger
the number, the closer the particular library was to the platin-
num target and further from the ITO target. Libraries located
closer to the ITO target resulted in an ITO-rich nanocom-
posite and since ITO has a large negative TCR, the nanocom-
posite reflected a negative TCR (See #1 trace in FIG. 4). The
libraries further away from the ITO target showed a dramatic
decrease in TCR (See #2-#5 trace in FIG. 4). However, when the
libraries were too close to the platinum target, platinum
dominated the electrical behavior and the sensor became
over-compensated. Since platinum has a large positive TCR,
the overall TCR of the sensor became positive (See #4-2 and
#5 trace in FIG. 4). A minimum in TCR was observed for
ITO-Pt combination between #4 and #4-2, which exhibited
small negative and positive TCR's (~79 and +50 ppm/° C.
respectively).

To determine the chemistry of the sensors, EDS analysis of
the most promising combinations was performed. Chemical
analysis and TCR of a number of ITO-Pt sensor combinations
are listed in Table 1. The absolute value of TCR decreased
dramatically with decreasing ITO content, and then increased
again when platinum content of the sensors dominated the
electrical properties. The results also indicated an optimal
nanocomposite sensor was combined with 88 wt % platinum and
12 wt % ITO wherein a very low TCR (+50 ppm/° C.)
strain gage could be produced with these percentages of mate-
rials or a 50 vol % ITO and 50 vol % Pt.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4-1</th>
<th>#4-2</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO wt %</td>
<td>28.2</td>
<td>22.6</td>
<td>19.4</td>
<td>11.2</td>
<td>12.0</td>
<td>16.0</td>
</tr>
<tr>
<td>TCR (ppm/° C.)</td>
<td>-2538</td>
<td>-1980</td>
<td>-1119</td>
<td>-247</td>
<td>-315</td>
<td>-155</td>
</tr>
<tr>
<td>calculated*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1

Chemical analysis and TCR of the nanocomposite sensors.
TABLE 1-continued

<table>
<thead>
<tr>
<th>Chemical analysis and TCR of the nanocomposite sensors.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID</td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td>TCR (ppm/°C) measured</td>
</tr>
<tr>
<td>-1755</td>
</tr>
</tbody>
</table>

Values were based on the model presented in O.A. Vasilievko, A.A. Maier, V.A. Chuskin, E. N. Gulaeva and V. I. Baro, J. Engineering Physics, vol. 49, issue 3, pp. 1185-1188, (1985).

Since some refractory metals exhibit larger, positive TCR’s than platinum (Table 2), other refractory metals were combined with semiconductors such as ITO in a single material at very small length scales to minimize apparent strain. Since less material would be required in the composite to cancel the effects of the large negative TCR of the oxide semiconductor, nanocomposite thin film strain gages based on ITO and other refractory metals were prepared to exploit the larger TCR’s of the refractory metals in an attempt to maximize the piezoresistive response. However, these non-optimized refractory metal combinations were more prone to oxidation and yielded less reproducible electrical properties including TCR relative to platinum (Table 2).

TABLE 2

<table>
<thead>
<tr>
<th>Thin film material</th>
<th>TCR (ppm/°C)</th>
<th>Temperature range (°C)</th>
<th>ITO-metal nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>-1800</td>
<td>&lt;1500</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>+1525</td>
<td>&lt;1400</td>
<td>near zero TCR @ 500-1200° C, not linear</td>
</tr>
<tr>
<td>Palladium</td>
<td>+1667</td>
<td>&lt;1200</td>
<td>hysteresis found at 800° C, not linear</td>
</tr>
<tr>
<td>Nickel</td>
<td>+2225</td>
<td>&lt;700</td>
<td>oxidation at 700° C, not stable</td>
</tr>
<tr>
<td>NiCoCrAlY</td>
<td>+1600</td>
<td>&lt;820</td>
<td>300 ppm/°C @ 100-800°C, TCR can be further reduced</td>
</tr>
<tr>
<td>Indium</td>
<td>+2280</td>
<td>&lt;880</td>
<td>not measured</td>
</tr>
<tr>
<td>Tungsten</td>
<td>+1825</td>
<td>&lt;550</td>
<td>not stable at above 550° C</td>
</tr>
</tbody>
</table>

Film thickness is approximately 1.5 µm.

Based on the above observations, the platinum dominated strain sensors yielded relatively low TCR’s. However, it was anticipated that the platinum contribution to the overall TCR of the nanocomposite may partially cancel the relatively large piezoresistive response associated with ITO. If the contribution of the platinum to the overall piezoresistive response were relatively small, it was anticipated that a nanocomposite strain sensor with lower TCR’s of the ITO alloy could be fabricated to yield a more stable strain gage response. The optimized ITO-Pt low TCR strain gage is listed in table 3.

TABLE 3

<table>
<thead>
<tr>
<th>Chemical composition of elements in the nanocomposite sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Pt</td>
</tr>
<tr>
<td>In</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Thus one could manufacture a thin film strain gage from a nanocomposite having a nominal composition in the range of 0.5 to 10.0 wt % ITO and 88 wt % Pt with preferred ranges of 12 wt % ITO and 88 wt % Pt or a 40 to 60 vol % ITO and 40 to 60 vol % Pt, with preferred ranges of 50 vol % ITO to 50 vol % Pt. The nanocomposite is deposited onto a substrate of substrate aluminum oxide or an aluminum oxide coated superalloy substrate, an aluminum oxide coated refractory metal substrate, an aluminum oxide coated stainless steel substrate or a thin monolithic ceramic substrate that is capable of being flexed. The nanocomposite can be in the form of a 100 µm thick, with a preferable thickness in the range of 0.1 um to 20 um thick.

The results also indicated that a nanocomposite sensor with the lowest TCR was achieved with 10 wt % ITO and 90 wt % platinum.
about 98% weight ZnO and about 2% weight alumina wherein the weights being based on the total weight of the AZO alloy.

The substrate of the thin film strain gage sensor may also comprise a thin metal, ceramic or composite substrate or flexible diaphragm containing one or more transducers to measure deflection of the flexible diaphragm. Such a flexible diaphragm prepared with one or more transducers could be used to measure deflection and thus, be correlated with pressure or force and be used as the active element in pressure sensors.

One can not purchase a pressure sensor which functions at temperatures above 450° C. as silicon or silicon carbide based electronics can not operate above 450° C. However by using self compensation attributes of the low TCR nanocomposite strain gages described within this invention to manufacture the active strain gage elements in such a pressure sensor, the pressure sensor will be able to function at temperatures well above 450° C. if the components comprising the body and diaphragm of the pressure transducer are made from refractory materials, a pressure sensor capable of operating at temperatures above 1400° C. is possible. The reason for the need of a low TCR nanocomposite strain gage in said applications is that temperature compensation in these types of pressure transducers is normally done using on board electronic compensation techniques, since the strain gage elements have too high a TCR for stable calibration and reproducibility of displacement of the diaphragm with pressure in the pressure transducer. In pressure sensor applications, the chemistry of the nanocomposite can be tweaked to yield the desired on board strain gage characteristics in terms of apparent strain effects.

A pressure sensor capable of functioning at temperatures above 450° C. can be manufactured. The pressure sensor comprises a thin metal, ceramic or composite flexible diaphragm which is electrically isolated from one or more thin film strain gages placed on the surface usually in a Wheatstone bridge configuration to measure small deflections of the flexible diaphragm. Based on these resistance changes, which are correlated with pressure or force, the pressure transducer is calibrated for a range of pressures. The low TCR nanocomposites (based on ITO and refractory metal) can be used as the active strain elements in the pressure sensors. The flexible diaphragm is typically welded or screwed into the housing (transducer body) which consists of a tube (or hollow cylinder) such that the strain gages deposited on the flexible diaphragm are facing the tube or housing, such that they never superalloy substrate, an aluminum oxide coated refractory composites (based on ITO and refractory metal) can be used as the substrate.

The substrate of the thin film strain gage sensor may also comprise a thin metal, ceramic or composite substrate or flexible diaphragm containing one or more transducers to measure deflection of the flexible diaphragm. Such a flexible diaphragm prepared with one or more transducers could be used to measure deflection and thus, be correlated with pressure or force and be used as the active element in pressure sensors.

The pressure sensor comprised of a low TCR nanocomposite film comprises about 90-97% weight In 2 O 3 and about 10-3% weight SnO 2 wherein the weights being based on the total weight of the ITO alloy.

The strain gage sensor of claim 1 wherein said ITO alloy comprises about 80-97% weight In 2 O 3 and about 20-3% weight SnO 2 wherein the weights being based on the total weight of the ITO alloy.

The strain gage sensor of claim 1 having a TCR in a range of +30 ppm/° C. to —30 ppm/° C. over a temperature range 25°C-1400° C.

The pressure sensor capable of functioning at temperatures above 450° C., said pressure sensor comprising: a substrate, a nanocomposite film comprised of an indium tin oxide alloy, zinc oxide doped with alumina or other oxide semiconductor and a refractory metal selected from NiCrAlY and NiCoCrAlY deposited on said substrate to form an active strain element, said strain element being responsive to an applied force.
a housing having a surface,
one or more thin film strain gages, each comprising ITO/
NiCoCrAlY,
a thin metal, ceramic or composite flexible diaphragm
which is electrically isolated from the one or more thin
film strain gages placed on the surface in a Wheatstone
bridge configuration to measure small deflections of the
flexible diaphragm.