Thermoelectric Properties of Ceramic Thin Film Thermocouples

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ABSTRACT

Thin film ceramic thermocouples are being developed to assess temperatures beyond 1400°C in the hot sections of gas turbine engines. Several promising ceramic materials were systematically investigated as thermoelements including indium-tin-oxide (ITO), alumina doped zinc oxide (ZnO) and a NiCrCoAlY/alumina nanocomposite. These ceramic thermoelements were initially tested relative to a platinum reference electrode and the resulting thermoelectric properties were evaluated. Bi-ceramic junctions comprised of the most stable and responsive ceramic thermoelements, i.e. those thermoelements with the largest and most stable Seebeck coefficients relative to platinum, were fabricated and tested. Bi-ceramic junctions based on nitrogen-doped ITO:oxygen-doped ITO exhibited excellent high temperature stability and reproducibility, however, this thermocouple pair had a relatively low Seebeck coefficient (6µV/°C). Alumina doped ZnO:ITO thermocouples generated a very large electromotive force at low temperatures but lacked high temperature stability. When nitrogen-doped ITO was combined with a NiCoCrAlY/alumina nanocomposite, a very large and stable Seebeck coefficient (375 µV/°C) was realized. Ceramic thermocouples based on these materials were demonstrated at temperatures up to 1200ºC and the potential for temperature sensors and energy harvesting for the production of electrical energy at a remote location with minimal processing is discussed.

Key words: indium tin oxide (ITO), alumina doped zinc oxide, NiCoCrAlY/alumina nanocomposite, ceramic thermocouple

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INTRODUCTION

The development of propulsion systems employing advanced materials and designs requires the continuous, in-situ monitoring of engine components operating under extreme conditions. Sensors capable of providing reliable data within the harsh environment of the gas turbine engine are needed for verification of structural models and engine health monitoring. The latter is becoming particularly important since higher temperatures can severely influence reliability, lifetime and performance issues of the respective components [1]. For example, the assessment of the temperature distribution or pattern factor in a gas turbine engine combustion chamber is critical since the lack of proper fuel burning can severely damage the components comprising the chamber. In order to meet the long-term instrumentation needs associated with engine health monitoring in harsh environments, robust thin film thermocouples and strain gages are being developed [1,2].

Thin film sensors are well suited for these strain and temperature measurements since their negligible inertial mass has minimal impact on vibration patterns and will not be affected by the high g-loading associated with rotating components [3-7]. In addition, thin film thermocouples have negligible thermal mass and thus, are more responsive than wire thermocouples. They also provide a more accurate measurement of the actual surface temperature [6,7]. Since these sensors are directly deposited onto a component, the sensors are in intimate contact with the component's surface and no adhesives are required. In addition, their thickness will not adversely affect gas flow through the engine [8, 9].

Ceramic thermocouples have certain advantages over precious metal thermocouples typically used in the gas turbine engine environment, when deposited in thin film form. These include little or no electromigration, a high melting point and chemical stability at elevated temperatures. The aforementioned ceramic thermocouples do not undergo phase changes and have a large and stable Seebeck coefficient when thermally cycled between room temperature and 1500°C. Furthermore, these ceramics are more oxidation resistant than metals and are not as costly as platinum and rhodium based thermocouples. In addition to these properties, their superior chemical stability at elevated temperature makes ceramic sensors promising candidates for other electrical devices at temperatures up to1500°C [1].

The most promising ceramics in terms of anticipated thermoelectric properties are indium tin oxide (ITO), zinc oxide (ZnO) doped with alumina and a nanocomposite based on NiCoCrAlY and aluminium oxide. Since ITO-based sensors have been successfully developed for strain measurement of engine components at temperatures up to 1500°C [10, 11] in air ambients, the aim here was to develop compatible temperature sensors and/or a means of producing electrical energy at remote location on a turbine blade for energy harvesting.

The approach taken here was to optimize the preparation parameters used to fabricate the ceramic (ITO) thermoelements with respect to thermoelectric response (Seebeck coefficient). Based on the resulting thermoelectric properties of ITO thin films relative to platinum reference elements, bi-ceramic junctions were prepared and tested. The composition of ITO based thermoelements was optimized in an effort to maximize the thermoelectric response, which is directly proportional to the applied temperature gradient according to the following equation:

$$V = k \cdot \Delta T \tag{1}$$

where ΔT = applied temperature gradient and k = Seebeck coefficient

As shown in equation (1), the output is influenced by the material constant k and the Seebeck coefficient or thermoelectromotive force [12, 13]. Since the thermoelectric power among others things is dependent on the composition of the thermoelements, the thermoelectric properties were systematically investigated as a function of process parameters.

EXPERIMENTAL DETAILS

To investigate the use of ceramic thermoelements in thermocouples and other thermoelectric devices, thin films were deposited on high purity (98.6%) alumina substrates. Rectangular beams measuring 6 inches by 1 inch were laser cut by International Ceramic Engineering. All reactively sputtered films were deposited in an MRC 822 machine whereas all rf sputtered films were deposited in an MRC 8667 sputtering system. Prior to deposition of the ceramic films, the substrates were rinsed in methanol, ethanol and deionized water, dried in dry nitrogen and coated with a layer of high purity alumina (Al_2O_3). This was done to prevent diffusion of ionic impurities from the substrate and promote better adhesion. The electrical properties of the thermoelements were more stable as a result of the adhesion layer [4]. The alumina was sputtered in an atmosphere of pure argon (9mtorr) using a high purity alumina target (99.99%) and had a nominal thickness of 0.2µm. After alumina deposition, the substrates were heated to 800°C to densify the films and to further enhance the bonding between the coating and the substrate as well as eliminate residual stress and point defects in the films. Adherent platinum films were subsequently sputtered using of a high purity 6-inch platinum target (99.99% pure) and were used as the reference electrode in all thermocouples as well as ohmic contacts to the ceramic sensors. They were prepared by placing an aluminium shadow mask over the alumina substrates to create the desired thin film patterns. The platinum elements were sputtered at an rf power of 350Watts and 2000 Volts in 9mtorr argon.

All ITO films were prepared by rf sputtering at 350 watts (power density of 1.38 W/cm^2) and 1800 volts. A background pressure of 10^{-6} torr was maintained in the vacuum chamber prior to sputtering and a high-density ceramic target (6 inch diameter) with a nominal composition of 90 wt% In_2O_3 and 10 wt% SnO_2 was used for all ITO depositions.

To investigate the electrical properties of the ITO thermoelements prepared under different sputtering conditions, the oxygen and nitrogen partial pressures were systematically varied from zero to 3mtorr while the argon partial pressure was maintained at 9mtorr. The effect of film thickness on thermoelectric response was investigated by varying deposition time.

The aluminum doped ZnO thermoelement was deposited from a 2-inch diameter target and the cermet consisting of 20 wt% Al_2O_3 and 80 wt.% NiCoCrAlY nanocomposite was deposited from a 4-inch diameter thermally sprayed composite target. Sputtering powers of 150 and 300 W were used for ZnO depositions to achieve power densities comparable to those used for ITO deposition.

The thickness of the deposited thin film was measured using a DEKTAK II profilemeter. After thin film deposition, the thermoelements were heat treated in a nitrogen-rich environment to remove residual argon trapped inside the deposited film. The ceramic samples along with a process monitor were heated to a temperature of

850°C at a rate of 3°C/hr. To evaluate the electrical properties, the furnace was maintained at 850°C at which point the temperature was held for 300 minutes and cooled to room temperature at the same rate. The resistivity was measured in the as-deposited and heat treated condition. After heat treatment the thermocouples were then placed into the 7-inch hot zone of a Deltech tube furnace where a temperature gradient was applied along the sample. In order to increase the temperature difference between the hot and cold junctions, a heat shield was placed in the middle of the sample as shown in Figure 1. The furnace was heated to temperatures on the order of 1350°C at a heating rate of 3°C/min and held for 60 minutes to establish thermal equilibrium and then cooled to room temperature at the same rate. All electrical measurements were done in air. The hot and cold junction temperatures as shown (Figure 1) as well as the generated emf were monitored by a USB data acquisition system (Personal DAQ 54 by I/O Tech) and associated software (Personal DaqView). Type S thermocouples were used to record the temperatures at the respective locations of the sample, as well as the thermocouple output (generated emf).

RESULTS AND DISCUSSION

Preparation and characterization of ITO thin film thermocouples

Table 1 summarizes the preparation conditions used for the deposition of the ITO thermoelements in terms of O_2 partial pressure [mtorr], N_2 partial pressure [mtorr], and Ar partial pressure [mtorr]. An ITO/Pt thermocouple with the ITO element being prepared in an atmosphere containing 1.9mtorr O_2, 2.2mtorr N_2, and 9mtorr Argon is shown in Figure 2. The hot and cold (dark and light grey curve) junction temperatures along with the output voltage of the thermocouple (black curve) were recorded at a sample rate of 1/10 sec. The thermoelectric response shows a linear increase in voltage with respect to temperature up to 1200°C, where the heating rate starts to decrease, eventually reaching a peak output voltage of 52mV at a temperature of 1261°C and a temperature difference of 884°C. At temperatures up to 800°C, there was a negative deviation from the Type S thermocouple output, whereas beyond 800°C there was a positive deviation. Even though similar Seebeck coefficients were observed, during heating and cooling (i.e. temperature vs. voltage slopes) it was apparent, that there was both a positive and a negative deviation from linearity depending on temperature. This phenomenon was due to the interaction of electrons and phonons (quanta of lattice vibrational energy) in the ceramic elements. Phonon scattering from other phonons and from other impurities influence the flow of electrons along a thermal gradient and therefore, influence the emf produced by the device. The degree to which these phonons drag electrons is highly dependent on temperature. At low temperatures only a small voltage is generated thus, the interaction between electrons and phonons is very small and thus is represented by the negative deviation from the linear temperature profile. As temperature increases, more phonons become available and drag the electrons along the gradient. This results in an increase of the temperature/emf slope and temporarily a linear behaviour. At high temperatures, phonon-phonon interactions become dominant and electrons are no longer dragged along. This inhibits the flow of electrons causing the thermoelectric power to level out [14]. Due to this deviation from linearity, the Seebeck coefficient was approximated using a 3rd order polynomial for the heating and the cooling cycles of the experiment. This polynomial gives the relationship between the imposed temperature gradient (T) and the generated voltage (V) over the entire linear range during heating. Table 2 summarizes the terms in the polynomial (equation 2) used to describe the voltage/temperature behaviour for the heating and the cooling cycles of the various thermocouples tested.

$$V(T) = A \cdot T^3 + B \cdot T^2 + C \cdot T + D \qquad (2)$$

The electromotive force (emf) as a function of the imposed temperature gradient for an ITO element prepared in an atmosphere containing 1.9mtorr O_2, 2.2mtorr N_2, and 9mtorr Ar relative to platinum (Figure 2) shows that ITO prepared under these conditions showed little hysteresis between cooling and heating cycles indicating good electrical stability and a reproducible thermoelectric response. The Seebeck coefficient of the ITO:platinum thermocouple was reasonably large (82 µV/°C).

Figure 3 shows the thermoelectric response of an ITO/Pt thermocouple where the ITO element was prepared in an atmosphere of 1.2mtorr O_2, 3.1mtorr N_2, and 9mtorr Argon. The hot junction temperature (dark grey curve) increased and decreased linearly, and a linear thermal gradient was applied to the thermcouple. Here, the cold junction temperature was represented by the light grey curve. Only a small thermal gradient (176°C) was applied to the sample. Due to this small thermal gradient, an emf (black curve) of only 4.5 mV was ultimately achieved. Despite this small gradient, a Seebeck coefficient of 107 µV/°C was recorded over the temperature range 200-1200°C. The voltage output as a function of temperature showed an S shaped curve typical of a ceramic thermocouple with both negative and positive deviations from linearity during heating but a rather linear voltage response during cooling. The thermoelectric properties were evaluated in terms of the Seebeck coefficient using a 3rd

order polynomial during the increase and decrease of the thermal gradient and the values for A, B, C, and D in the equation (2) are shown in Table 2.

Table 3 summarizes the thermoelectric response of seven different ITO thermoelements prepared under different conditions relative to platinum. This table not only lists the Seebeck coefficients of a number of ITO films prepared under different conditions but also indicates any deviation from the Type S behaviour (+ and -). Also, the deviation of the sensor output from linearity is listed along with the deviation associated with poor sensor performance (- -) and small deviations from linear temperature profile (+). The assessment of thermoelectric properties in terms of Seebeck coefficients in general is very difficult since complex polynomial functions are usually used to describe the thermoelectric response to an applied temperature gradient. This proved to be the case in this study, since the calculated coefficients for the different ITO compositions varied greatly and in some cases even the sign of the coefficient changed depending on the temperature range. The Seebeck coefficients listed in Table 3 were based on the thermoelectric response over the temperature range 500-1000°C. The choice of suitable ITO thermoelements for bi-ceramic junction was made on the basis of high temperature stability and performance. The ITO composition prepared in pure argon was the most promising from this viewpoint, having little deviation from linearity at low temperatures and a reasonable voltage increase at elevated temperatures.

Characterization of ITO:ITO bi-ceramic junctions

The thermoelectric response of a bi-ceramic junction comprised of two ITO thermoelements sputtered in atmospheres containing 2.9mtorr O_2, 2.7mtorr N_2, and

9mtorr Argon and in a pure Argon atmosphere (9mtorr), is shown in Figure 4. A similar thermoelectric response was recorded for another bi-ceramic junction whose ITO thermoelements were prepared under atmospheres containing 9mtorr Argon and 2.7mtorr O_2, 2.2mtorr N_2, and 9mtorr Argon, respectively.

Characterization of ZnO for thin film thermocouples

One of the most promising semiconductor materials for high temperature sensor applications is ZnO. A ZnO film doped with Al_2O_3 was used to create a bi-ceramic junction with ITO. ZnO is a p-type semiconductor and when combined with an n-type semiconductor such as ITO, a very large thermoelectric response was anticipated. Figure 5 shows the thermoelectric response of a ZnO/Pt thermocouple, where the dark grey curve represents the hot junction temperature. Here, a maximum thermal gradient of 516°C was achieved at 1325°C with a maximum voltage (black curve) of 131mV being obtained for this thermocouple pair. A very similar thermoelectric response was observed for a ZnO/ITO thermocouple. Here, a linear increase in thermoelectric response was achieved in the presence of a small thermal gradient (527°C) and a maximum emf of 140mV was achieved.

In order to stabilize the output signal of thermocouple comprised of ZnO thermoelements at elevated temperatures, a protective alumina layer was sputtered over the elements. The thermocouples comprised of ZnO thermoelements showed unstable behaviour and various inflection points. As the thermal gradient was increased, the voltage rapidly increased but with continued heating the voltage decreased and finally disappeared.

Characterization of a nanocomposite based on NiCoCrAlY and aluminium oxide

A nanocomposite based on NiCoCrAlY and aluminium oxide was investigated as a candidate material for a robust ceramic thermocouple. Earlier studies of this material indicated that it exhibited poor thermal conductivity due to the large number of interfaces in the direction of heat transfer and associated phonon scattering. However, the material had reasonably good electrical conductivity due to the large metal content and thus, was an excellent candidate for thermocouples and thermoelectric devices. The TEM micrograph of the NiCoCrAlY/alumina nanocomposite (Figure 6) shows the alumina (black phase) uniformly distributed throughout the NiCoCrAlY matrix (grey phase) [16]. The phonon-electron interaction responsible for electron drag as described earlier does not occur in this predominantly metallic material and therefore no significant S-shaped thermoelectric response was observed. Initially, the nanocomposite film was tested relative to platinum and was combined with two different ITO thermoelements. These ITO elements were prepared in pure argon and pure nitrogen atmospheres, respectively and were heat treated in a nitrogen-rich atmosphere. The nano composite material itself was sputtered in 9mtorr argon and no post deposition heat treatment was necessary.

The thermoelectric response of the nanocomposite relative to platinum is shown in Figure 7. The voltage output (black curve) peaked at 145.6mV coinciding with the peak temperature of 1243°C and a temperature gradient of 915°C. At low temperatures, little voltage was generated by the thermocouple, suggesting that a threshold temperature of 700°C was necessary to achieve a response. Initially, a negative voltage was produced with significant scattering of data at low temperatures. As the temperature was increased, however, the voltage increased rapidly and the scattering in the data disappeared. Apparent in this thermocouple was the linear thermoelectric response compared to the ITO thermocouples, likely due to the large metal content in the material. However, different slopes associated with the thermoelectric response were observed as the temperature was increased and decreased. The relation between applied temperature gradient (T) and generated voltage (V) according to equation (2) for the nanocomposite is displayed in Table 4.

A Seebeck coefficient of 1400µV/°C was calculated for the heating cycle based on equation (2) and the thermocouple produced a signal with little scattering. In comparison, the Seebeck coefficients calculated for ITO/Pt thermocouples were 1-2 orders of magnitude smaller, suggesting that thermocouples comprised of a NiCrCoAlY/alumina nanocomposite were extremely responsive.

Figure 8 shows the thermoelectric response of a nanocomposite/ITO thermocouple with the ITO element prepared in pure nitrogen (9mtorr). A temperature difference between the hot and cold junctions of 639°C generated an emf (black curve) of 146mV. A threshold thermal gradient of 450°C and a hot junction temperature of 720°C were necessary to obtain a signal. Initially, some scattering of the data occurred at these lower voltages but the voltage increased, the scatter in the voltage/temperature behaviour disappeared. The output voltage tracked the Type S thermocouples and showed a linear increase and decrease corresponding to the heating and cooling cycles. The response to the decrease in temperature appeared to lag behind the Type S thermocouples. The high temperature performance of the thermocouple proved to be excellent, as indicated by tracking of the Type S thermocouples. During cooling, a negative voltage occurred as described in previous experiments and ultimately approached 0mV at 615°C and a thermal gradient of 335°C, respectively. A Seebeck coefficient of 375μV/°C for the heating cycle indicated that the combination of the nanocomposite and ITO did not only improve the high temperature performance but also improved the sensitivity at lower temperatures.

CONCLUSION

A systematic investigation of the thermoelectric properties of ITO as a function of its process parameters was made in an attempt to produce an all-ceramic thermocouple. Initially, ITO films were tested relative to platinum as a reference element. After initial screening, bi-ceramic junctions based on different ITO compositions were prepared and investigated as potential thermocouples that could survive the harsh environment associated with gas turbine engines.

The testing of ITO relative to platinum indicated that there was significant deviation from the linear applied thermal gradient with thermoelectric response in the range of 45mV - 63mV. Very stable results in terms of emf signal and sensitivity were observed at elevated temperatures, however, only a few ITO compositions actually tracked the temperature gradient. However, the bi-ceramic junctions comprising the two most promising ITO compositions produced very unstable signals and poor sensitivity.

A nanocomposite comprised of NiCoCrAlY and aluminium oxide was investigated and proved to be the most promising candidate for bi-ceramic thermocouples. The surfaces of the NiCoCrAlY exposed to air were passivated with Al_2O_3 giving the composite excellent high temperature stability in air. Unlike the ITO/ITO bi-ceramic junctions, the nanocomposite/ITO thermocouple tracked the temperature gradient at elevated temperatures and had Seebeck coefficients almost 2 orders of a magnitude larger than that of ITO/ITO thermocouples. Seebeck coefficients on the order of 375µV/°C as compared to 6 µV/°C were observed for the nanocomposite/ITO thermocouples.

One of the objectives of this study was to develop a ceramic thermocouple for high temperature measurements that could be integrated with ITO strain sensors. A thin film thermocouple with one thermoelement based on a nanocomposite (NiCoCrAlY and aluminium oxide) and the other based on ITO was developed for temperature measurements. The active ITO element developed for strain measurement was similar to the composition of ITO developed for temperature measurements. In this way simultaneous strain/temperature measurements could be made at the same location (at elevated temperatures) with minimal thin film processing.

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