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A Rugged Oxygen Gas Sensor with Solid Reference for High Temperature Applications

A. K. M. S. Chowdhury,[a] S. A. Akbar,[a,*,z] S. Kapileshwar,[a] and J. R. Schorr[b]

[a]*Center for Industrial Sensors and Measurements, The Ohio State University, Columbus, Ohio 43210, USA*
[b]*The Edward Orton Jr. Ceramic Foundation, Westerville, Ohio 43082, USA*

An oxygen sensor based on yttria-stabilized zirconia with Ni-NiO mixture as a solid reference electrode for high temperature applications has been fabricated and tested. During high temperature use Ni reacts with inner Pt electrode and Pt lead wire, and affects the output signal of the sensor leading to a limited lifetime. This is the first time an Al_2O_3 isolation layer has been introduced in the design of an oxygen sensor. Use of this isolation layer prevents high temperature alloy formation between Ni and Pt, leading to a significant enhancement in the performance and the stability of the sensor. The sensor shows fast response with good recovery characteristics in the temperature range of 600-1400°C. However, after repeated tests over a longer period, the sensor performance degrades possibly due to grain growth and sintering of the inner electrode at high temperature.
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The measurement and control of oxygen atmosphere inside a ceramic kiln are critical for the manufacture of useful ceramic products.[1] Yttria-stabilized zirconia (YSZ)-based oxygen sensors are being used for this purpose. Such sensors can only measure oxygen concentrations in an area very near the wall of the kiln, as the sensor uses an air reference electrode and the length of the zirconia tube limits the location of measurement. Also, in the application environment, the sensor encounters severe operating conditions, such as high temperature, large temperature fluctuations, mixtures of gases, heavy dusts and vapors, and thermal shock. Recognizing the influence of these factors, the sensor probes must be specially designed, particularly those using a solid reference electrode.

The use of a galvanic cell for the determination of oxygen concentration in liquid steel was developed in many countries during the decade 1960-1970.[2] At that time a number of metal-metal oxide mixtures (*e.g.*, Mo-MoO_2,Cr-Cr_2O_3, etc.) were employed to fix the reference oxygen in a YSZ cell. These cells were exclusively designed for one-time use and oxygen was measured by dipping them in the molten steel. As they were used for one time only, their long-term stability was not an issue. Note here that Cr[3] and Mo[4] react with Pt electrodes and form compounds at relatively lower temperatures. Compound formation eventually leads to an unstable sensor.

Solid reference gives an equilibrium oxygen partial pressure at the operating temperature. The main advantage of solid reference over the air is that the metal-metal oxide mixture inherently produces extremely low O_2 concentrations (trace) with respect to the test environment, thus producing a large pressure difference, leading to enhanced emf signals. If the partial pressure is too low, it is difficult to establish the equilibrium. If too high, the decomposition of metal oxide becomes significant. Thus, choosing a proper metal oxide reference electrode is very critical. Virtually this metal oxide acts as an oxygen pump, which provides a source of steady flow of oxygen. The partial pressure (p_{O_2}) generated by a given metal oxide can be determined by calculating the equilibrium constant for a given metal-metal oxide system.[5] For example, the partial pressure of oxygen generated by a Ni-NiO system is calculated to be of the order of 10^{-16} atm. at 250°C.[6] The sensor using a solid reference electrode can be represented by the following electrochemical cell

$$O_2,\ Pt/YSZ/Pt,\ M,\ M_xO_y$$

Here M is a transition metal, such as Ni, Bi, Mo, etc., and can be univalent or multivalent. In case of multivalent metal, M represents W, Fe, Cr, Mn, Ba, etc. In this study, Ni-NiO was used as the solid reference electrode. Other metal-metal oxide systems, such as Co-CoO were studied and found unstable at the operating temperature. Thermodynamic data for Ni-NiO/O_2 system is well established and is not presented here.

Based on the principle discussed above, preliminary work using Ni-NiO was carried out in the authors' laboratory that shows promise.[7] In that work the possibility of alloy formation between Ni and inner Pt electrode at relatively lower temperatures (around 700°C) was disregarded. At high temperatures, the Ni-Pt alloy formation[8] is highly likely that would result in the degradation of the inner electrode in the long-term. This article addresses this problem specifically and presents a design for measuring oxygen concentrations in the temperature range of 600-1400°C.

Experimental

Probe fabrication.—A typical oxygen sensor that was fabricated and tested can be represented as

(Sensing side) Pt electrode | YSZ tube (one end closed), Al_2O_3 isolation | Ni-NiO reference electrode | Pt electrode

Figure 1 shows the schematic of an oxygen sensor probe. A one-end closed YSZ tube (from Vesuvius McDanel; 12 mm o.d., 10 mm i.d., and 40 mm long) was used as the body of the sensor. Ni-NiO was used as the solid reference electrode due to its high exchange current of oxygen ion. Fine Ni metal powder (<100 mesh, Johnson Mathey Company) was treated by 5% H_2 in N_2 at 900°C to remove any surface oxide. Fine NiO powders (<100 mesh, Johnson Mathey Company) were treated at 1400°C for 1.5 h in air. For filling and isolation materials, Al_2O_3 fine powder (<325 mesh, Johnson Mathey Company) was used. Al_2O_3 powder was treated at 1500°C for 2 h in air.

Approximately two-thirds of the tube was filled with Ni-NiO mixture (9:1). Pt-Ni binary phase diagram[8] indicates formation of binary solid solution between Ni and Pt throughout the temperature range of 700-1400°C. This solid solution formation was verified experimentally by heat treating Ni and Pt powders (50-50 wt %), inside an evacuated glass tube at 1200°C. The treatment was carried out at 1200°C because of the glass tube used. The results can be extrapolated to 1400°C, as the phase diagram indicates that the same phase is formed at both temperatures (Ni-Pt solid solution). Using X-ray diffraction (XRD) as a diagnostic tool, alloy formation was confirmed. To avoid this alloy formation, Pt wire was isolated from the Ni-NiO mixture using an Al_2O_3 tube (Fig. 1). A portion of the YSZ tube was filled first with Al_2O_3 powder covering the Pt contact inside the YSZ tube giving virtual isolation of Ni-Pt contacts. The

* Electrochemical Society Active Member.
z E-mail: akbar.1@osu.edu

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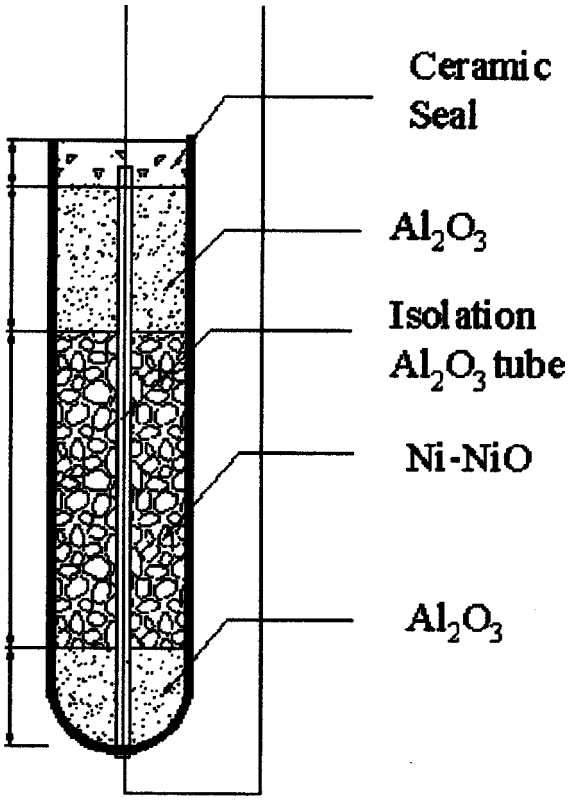

Figure 1. Schematic of the sensor probe showing the isolation using alumina.

rest of the tube was packed with Al_2O_3 powder to fill the space. The open end of the tube was sealed with a high temperature sealing material.

Heat-treatment of sealing material.—Two types of sealing materials were used: Resbond 989 and Resbond ceramic binder 794, Cotronics Corp. The first sealing material (989) is an Al_2O_3-based porous bonding material. The second sealing material (glass-based, 794) helps seal the pores giving a hermetic seal. After adding the bonding material (989 type) the sample was kept at room temperature for 4 h. After that, the sample was kept at 200°C for 4 h, 400°C for 4 h, 800°C for 2 h, and 1400°C for 1 h. A very slow heating and cooling rate (1°C/min) was employed to avoid cracking. After heat-treatment of the 989 type was done, 794 type was applied as an overcoat using a fine brush and kept at room temperature for 1 h. The samples were then heated to 79°C for 2 h, 176°C for 2 h, 315°C for 2 h, 600°C for 2 h, and 1400°C for 1 h. The same heating and cooling rates were employed for the 794 type.

Electrode preparation.—Pt ink (Engelhard Platinum ink) was painted on both sides of the closed-end tip of the YSZ tube. Fine mesh Al_2O_3 particles were mixed with the Pt paste in the green state to help form a mechanically stable electrode. For electrical connection, Pt lead wires were attached to the coated portions of the YSZ tube when the paint was in the green state. The assembly was kept in air for 2 h. It was then cured at 1250°C for 6 h. A heating and cooling rate of 5°C/min was maintained as recommended by the ink manufacturer. Typical ink contains 80% metal and 20% organic binder. These organic substances evaporate during heat-treatment and make the electrode porous; they play the key role as the ''gas-metal-oxide three-point contact.''

Sensor test procedure.—The fabricated sensors were tested in a tube furnace (1500°C Lindberg). The samples were placed at the center of an open-end quartz tube. This quartz tube was placed in the furnace. A constant gas flow was maintained with varying oxygen concentrations through the tube. Mass flow controllers calibrated before the experiments maintained gas flow. The electrodes of the sensor were connected to a HP multimeter and the corresponding emf at a certain temperature and oxygen concentration was recorded.

Table I. Comparison of the experimentally observed *d* values with those theoretically calculated from diffraction data.

Diffraction planes (*hkl*)	Calculated *d* value (Å)	Observed *d* value (Å)
100	2.140	2.09816
200	1.860	1.81906
220	1.316	1.28966

Characterization.—A Scintag PAD-V X-ray diffractometer was used for phase analysis. The instrument is fitted with a Cu anode, 2 kW sealed tube X-ray source. A Philips XL-30 FEG scanning electron microscope (SEM) was used to observe the morphology of the inner and outer Pt electrode. Chemical composition of the outer Pt electrode and the Ni-NiO/inner Pt electrode interface were analyzed by using energy dispersive X-ray (EDX) DX-4 with a sapphire detector having a super ultrathin window (SUTW) installed in the XL-30 FEG SEM apparatus. The EDX instrumental error is $<5\%$.

Results and Discussion

From the results of the XRD analysis on Ni-Pt powder mixture heat treated at 1200°C, it is seen that the peaks resulting from the solid solution lie in between the expected peaks for pure Ni and pure Pt. This is as expected with respect to a solid solution. Both pure Ni and Pt crystallize in the face-centered cubic (fcc) structure, with lattice constants of 3.5238 and 3.9231 Å, respectively. Vegard's law for a solid solution states that the lattice parameter for a substitutional solid solution depends on the weight fraction of each component, and is a weighted mean of the lattice constants of the two components. Accordingly, the lattice constant for a 50-50 wt % Ni-Pt solid solution would be the arithmetic mean of the lattice constants of pure Ni and pure Pt, and is estimated to be 3.72385 Å. Using this lattice constant, *d* values for the corresponding lattice planes in an fcc crystal were calculated. These *d* values were then compared with the observed *d* values from the diffraction pattern. As listed in Table I, within experimental uncertainty, the calculated and the observed values match reasonably well. Based on this agreement, along with the fact that the peaks in the diffraction pattern lie

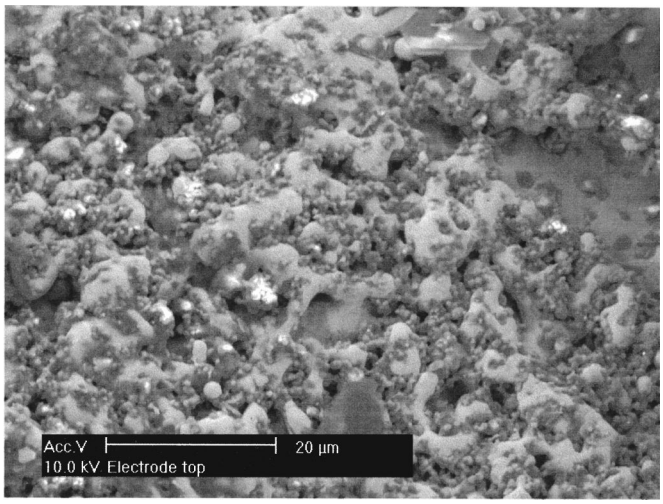

Figure 2. SEM image showing outer Pt electrode. Dispersed Al_2O_3 particles are also observed.

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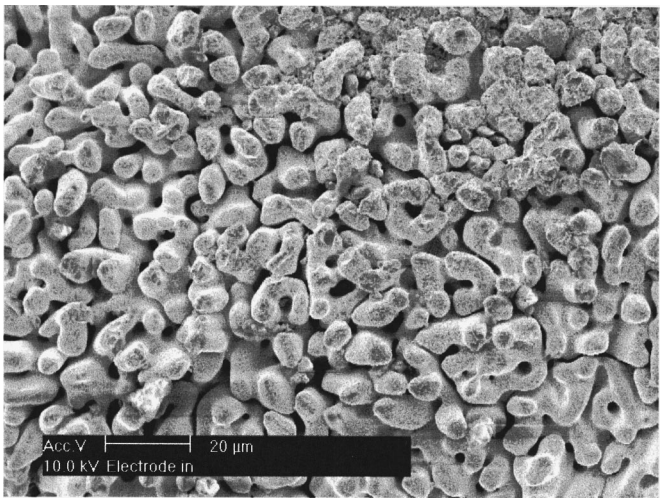

Figure 3. SEM image showing the inner electrode with evidence of grain growth and sintering.

in between the peaks for pure Pt and pure Ni, we can conclude that a solid solution is formed between Ni and Pt at the heat-treatment and working temperatures of the sensor.

Figure 2 shows the SEM image of the outer Pt electrode tip. The outer Pt electrode is porous and dispersed Al_2O_3 particles can be observed. These powders were mixed with the Pt paste in the green state. During curing of the Pt paste, these powders help formation of mechanically stable electrode. Figure 3 shows the SEM image of the inner Pt electrode. The inner Pt electrode is morphologically different from the outer one, although the same Pt paste was used for electrode preparation. The inner electrode is also porous, but there is evidence of grain growth and sintering. During Ni and NiO powder mixing, NiO was dispersed in such a manner that some of it was agglomerated. This agglomerated NiO is seen in several locations on the inner Pt electrode as evident in the micrograph (Fig. 4). As Ni forms solid solution with Pt, the Ni part in the original Ni-NiO mixture becomes less at the interface leaving these NiO chunks on Pt-Ni alloy surface. The dispersion of NiO directly on Pt surface along with grain growth at a high temperature of operation would change the inner electrode characteristics from the outer one, making the sensor unstable.

To prevent the interaction of Ni with Pt, and thus avoid solid solution formation, Pt wire was isolated from the Ni-NiO mixtures

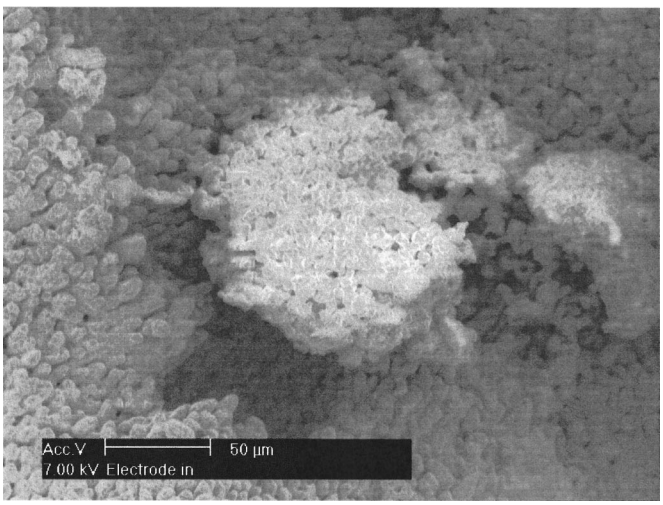

Figure 4. SEM image showing NiO on top of the inner Pt electrode.

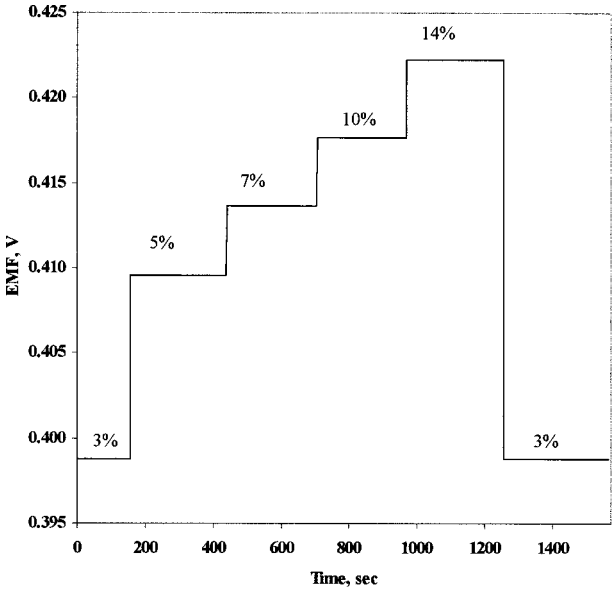

Figure 5. Response characteristics of a stable sensor at 1200°C at different oxygen concentrations.

using an Al_2O_3 tube. Figure 5 shows the response characteristics of the sensor having isolation between inner Pt electrode and Ni-NiO solid reference at 1200°C. The data show good response and recovery characteristics. The 90% response time is as short as a few seconds and the recovery time is less than 20 s.

Figure 6 shows the emf signal as a function of oxygen concentration (logarithmic scale) showing the Nernstian behavior of the sensor at 1200°C. The theoretical values estimated based on the Nernst equation and the experimental data are shown. It can be seen from the figure that whereas the slopes are practically identical, the experimental and theoretical data are offset by a constant amount. This is because practically it is difficult to prepare identical Pt electrodes on the inner and outer surfaces of the YSZ tube. These dissimilar Pt surfaces produce the observed difference in the numerical values.

Figure 7 shows the response of the sensor along with reversibility behavior at 1400°C. This response along with those observed at 1200°C indicates that the sensor is leak free and shows good response characteristics up to 1400°C in the short term. However, after repeated tests over a longer period, the sensor performance degraded. A noticeable amount of drift was observed in the sensor signal, when the sensor was continuously tested at 1250°C in air over 3.5 days. The output voltage drifted at the rate of about 5 µV/min. This drift possibly arises due to grain growth and sintering of the inner electrode. So, in addition to isolating the metal/metal oxide mixture from Pt, one must find a system that does not sinter at the operation temperature.

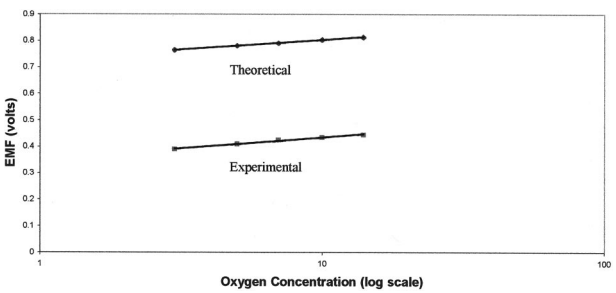

Figure 6. Comparison of the theoretical and experimental data at 1200°C showing the Nernstian slope.

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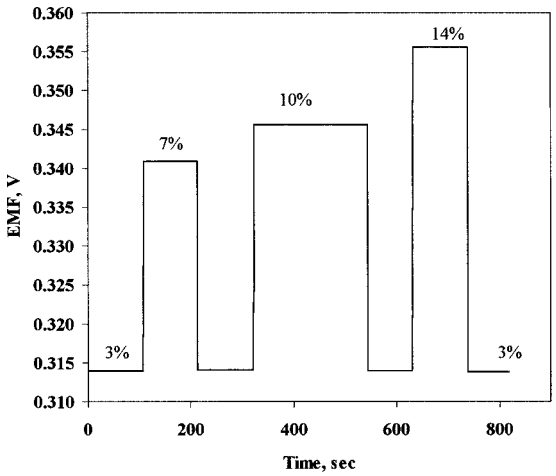

Figure 7. Response and reversibility test of an oxygen sensor at 1400°C.

Conclusions

For high temperature (in the range of 600-1400°C) use, an oxygen sensor based on a solid reference electrode using Ni-NiO has been designed and tested. An optimized heat-treatment procedure has been developed for curing of electrode and sealing materials. The response and recovery are fast with 90% response time as short as a few seconds and recovery time < 20 s. The sensor shows a Nernstian response with a constant offset in signal magnitude due to dissimilar electrodes formed during Pt paint curing on the two sides of the closed-end YSZ tube. Metal-metal oxide (Ni-NiO) solid reference oxygen sensors become unstable and cannot be considered for long-term use due to formation of Pt-Ni alloy. To avoid this alloy formation Pt lead wire and electrode were isolated from the Ni-NiO mixture by using ceramic isolation (Al_2O_3). The sensor with the isolation gives stable performance in the temperature range of 600-1400°C in the short term. It also gives considerably stable results in the long term up to about 1000°C. However, the sensor suffers from long-term stability at temperatures in the range of 1200-1400°C, possibly due to grain growth and sintering of the inner electrode. So, in addition to isolating the metal/metal oxide mixture from Pt, it is necessary to find a system that does not sinter at the operation temperature.

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