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Spielberg et al.

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[54] **OXYGEN SENSOR FOR AUTOMOTIVE USE**

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[51] **Int. Cl.²** **G01N 27/46**

[58] **Field of Search** ..... 204/195 S, 1 T; 324/29

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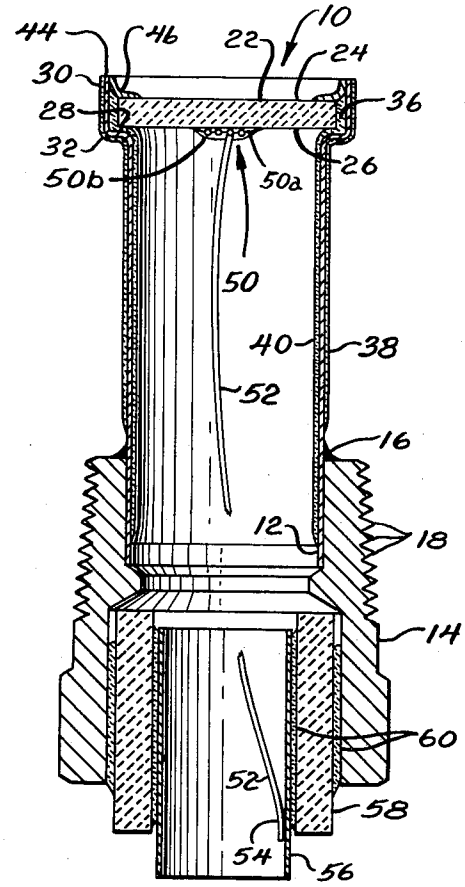
[57] **ABSTRACT**

Oxygen sensor for automotive use utilizes a disc shaped wafer of a solid electrolyte, preferably zirconia stabilized with MgO, which is extremely resistant to abrasion and the effects of repeated temperature excursions over long periods of use. The housing comprises a hollow metal tube stepped at one end to support the electrolyte wafer and hermetically sealed to the wafer by a metal oxide frit which is melted in a vauum. The electrodes comprise a thick film Ag - Pd alloy which is bonded to the wafer by means of a glass forming binder.

8 Claims, 3 Drawing Figures



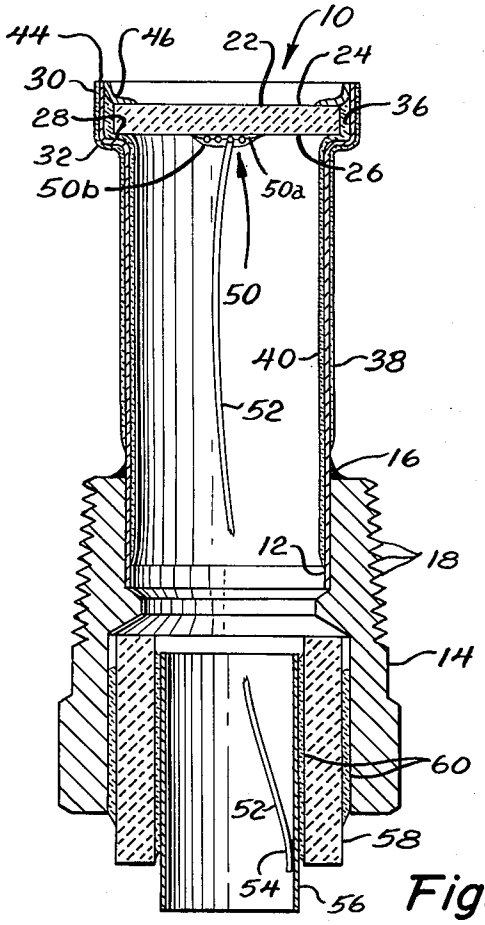


Figure 1

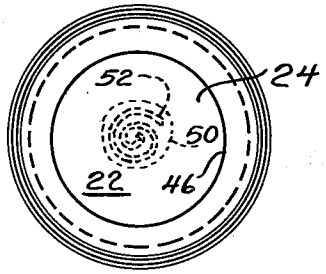


Figure 2

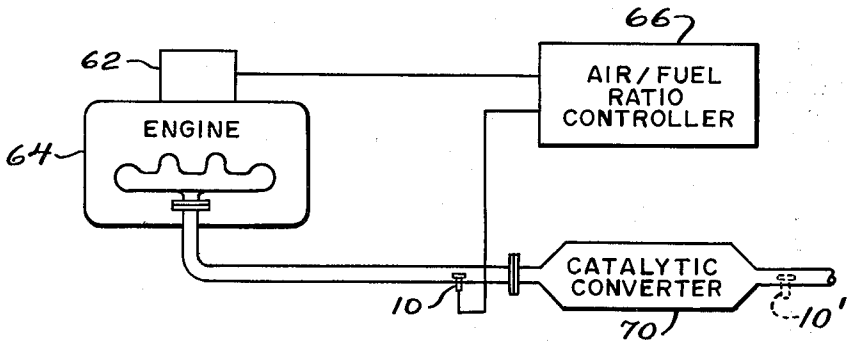


Figure 3

OXYGEN SENSOR FOR AUTOMOTIVE USE

BACKGROUND OF THE INVENTION

An increasing concern to protect the environment from various sources of pollution has led to the setting of limits on the emissions of various noxious exhaust gas elements which can be permitted to emanate from an internal combustion engine. Since oxides of nitrogen are formed under different engine operating conditions than carbon monoxide and excess hydrocarbons, much consideration has been given to ways of reducing all three noxious elements to a satisfactory level. One way to accomplish this goal is by running the engine rich and passing the exhaust gases through a first catalyst to reduce the nitrogen oxides and then adding secondary air to the exhaust gases and passing them through an oxidizing catalyst to convert the carbon monoxide and hydrocarbons to carbon dioxide and water. The dual catalyst system is not only relatively costly in the equipment which it requires but is also quite wasteful of fuel. It has been found that a single catalyst is capable of controlling all three exhaust components if the engine can be operated with an air/fuel ratio which is stoichiometric or just on the rich side of stoichiometric. Unfortunately, the carburetors and fuel injection systems which are presently available cannot continually deliver a precise air/fuel ratio to the engine under varying operating conditions.

Solid electrolyte oxygen sensing cells which produce a voltage indicative of the difference in oxygen partial pressures between the sampling side of the cell and the reference gas (usually air) side of the cell have been used for many years. In recent years, various attempts have been made to adapt these units to automotive use since the cells have the property of undergoing a very large change in voltage output when the air/fuel ratio of the exhaust gases they contact moves from one side of stoichiometry to the other. By utilizing an oxygen sensor in combination with a closed loop control system it is possible to control the fuel or air input to the engine or to the catalytic converter so that the air/fuel ratio can be precisely controlled.

Although the advantages of using oxygen sensors as an aid in controlling engine emissions are well known, those persons working in the art have experienced great difficulty in producing a sensor which can, for long periods, withstand the extremely hostile environment of an automotive exhaust system. For example, a sensor should be able to withstand continual temperature changes from as low as −50°F to 1500°F with occasional temperature spikes of an even greater temperature. The sensing element and seals should have sufficient thermal shock resistance to withstand heating from −50°F to 700°F in about 1 second. The sensor should be resistant to poisoning by lead, sulfur and phosphorus, should have a thermal expansion coefficient capable of permitting its seals to withstand continual temperature cycling for 25,000 miles or more of engine operation, and should be impervious to prevent gas leakage from its sampling side to its reference side. Furthermore, it should respond very quickly to produce a voltage output which can be used to produce almost instantaneous corrections in the engine air/fuel ratio. Finally, it should be low in cost, compact, vibration resistant, and easy to mount and remove.

Because of the rugged nature of an automotive exhaust environment as compared to a flue or stack, for example, oxygen sensors which are suitable for the latter use are not suitable for automotive use. Most prior art oxygen sensors utilize heating elements to maintain the solid electrolyte cell at a sufficiently high temperature (over about 750°F) for it to produce a voltage. Such sensors are not only bulky but also expensive. Although a wafer type solid electrolyte oxygen sensing cell is disclosed in East German Pat. No. 21,673, it is quite unlikely that the spring biased seal provided for the wafer to isolate the outer sampling side from the inner reference side would be effective to prevent leakage of gases from the sampling side to the reference side if the sensor were used in an automotive exhaust system. The usual form of the solid electrolyte for automotive type oxygen sensors has been thimble shaped. This choice has no doubt been made, even though a thimble shape would be far more expensive and difficult to form as compared to a flat shape, for the reason that it has been thought that it would be extremely difficult, if not impossible, to provide an effective and durable hermetic seal using a flat shape. A hermetic seal is necessary since the solid electrolyte produces a voltage in accordance with the difference in oxygen partial pressures on its two sides. Obviously, a leakage of gases will produce an incorrect voltage. The problem is relatively minor where the leak is small and the composition of the sample gas is constantly changing. However, when the engine is running in a steady state condition, any leak can be important, especially since it is generally desirable to have no more than a very limited circulation of the reference gas in order to maintain the gases on each side of the electrolyte at the same high temperature.

The material most commonly used for the solid electrolyte is zirconium dioxide mixed with a stabilizing metal oxide such as that of calcium or yttrium to provide a solid solution of ionically conductive oxides, as discussed in copending application Ser. No. 159,936, now U.S. Pat. No. 3,768,259, assigned to a common assignee. Although, U.S. Pat. No. 3,365,317 discloses a stabilized composition of zirconia and magnesium oxide, the composition is not disclosed for use as a solid electrolyte, but, rather, as a material for an extrusion die. U.S. Pat. No. 3,503,809 mentions magnesium oxide as one of several materials which could be used to stabilize a solid electrolyte for use in a fuel cell but seems to rely on calcium oxide as the stabilizing agent.

SUMMARY

It is among the objects of this invention to provide a rugged, durable, and economical oxygen sensor for use in an automotive exhuast system.

Although certain of the individual structural features of our improved sensor have been used before, the particular combination of features of the embodiment disclosed herein provides a sensor which appears to be far superior to prior sensors. The sensor comprises a housing portion formed of a short length of metal tubing and an externally threaded metal body portion to which the tubing is welded. Preferably, the tubular housing member is of Series 409 stainless steel or other high temperature, highly corrosion resistant material. The threaded portion may be of the same material or another, such as Series 304 stainless. The inner end of the sensor housing (the sensing end which extends into the exhaust path) is formed with a shelf or shoulder so as to provide a recessed seat for a disc shaped wafer of solid

electrolyte. The shelf can be formed by boring out a short axial portion of the inside of the tubing or by expanding the end of the tubing to a greater diameter than the remainder of the tubing. The threads on the body portion are preferably male pipe threads, similar to those on a spark plug, which are adapted to engage female threads formed in one of the portions of the engine exhaust path.

Mounted on the shoulder portion of the sensor housing, and hermetically sealed thereto, is a wafer of stabilized zirconia which performs as a solid electrolyte. Yttria and calcia stabilized zirconia wafers have excellent electrical properties, such as a relatively low resistance, and have been used as solid electrolytes. However, they appear to be vulnerable to wear from particles present in the exhaust stream and to cracking caused by the extreme thermal stresses during the start-up of an automotive engine. Although it is believed that it has not previously been used as a solid electrolyte in an oxygen sensor, zirconia stabilized with a small amount of magnesia (about 3%) has been used as an extrusion die material (U.S. Pat. No. 3,365,317) which exhibits superior thermal shock capability. For example, a red hot piece can be plunged into ice water without cracking. Wafers of magnesia stabilized zirconia produced by the Zircoa Division of Corhart Refractories Company of Solon, Ohio, as Zircoa Composition No. 1027, have been hermetically sealed to a pre-oxidized Series 409 stainless steel tubular housing by means of a green, semi-glossy frit material (No. SL-14230C manufactured by Thomas C. Thompson Company and sold by Chicago Vitreous Corporation of Cicero, Illinois) containing a mixture of CrO_3, TiO_2, and SiO_2. The tube is preferably dipped over its entire length to provide as much protection as possible against corrosion. The tube, with the zirconia wafer in its end recess, is then fired in a vacuum for 15 minutes at 1900°F to fuse the sealing material to the tube and to the wafer and to degas it. The degassed seal is then subjected to atmospheric pressure at temperature to form a void free seal. Subjection of the aforementioned wafer, tube and sealing material to road testing has indicated that the integrity of the seal can be maintained for more than 15,000 miles when only the wafer end of the tube is coated. The seal life should be substantially higher when the entire length of the tube is coated and protected against corrosion, such as might be caused by road salt entering the reference end of the sensor.

The cell EMF is measured between a pair of electrodes attached to its opposite surfaces. A suitable electrode material appears to be a paste comprising an alloy of about 56.4 parts of silver powder and 14.1 parts of palladium black in a glass forming binder which is sold by Electro Materials Corporation of America, Mamoroneck, N.Y., as "Firon" No. 618. The electrode material is first applied to the center of the reference side of the electrolyte wafer and fired for 1 hour at 1700°F. A lead wire is then attached to the wafer with additional electrode material and the composite is then fired at 1700°F for 15 minutes to firmly affix the lead wire. The sampling side electrode, which is fired at the same time as the reference electrode, is annular in shape and bridges the wafer and the outer end edge of the tubular housing. The frit coating is removed from the end of the housing before the electrode is applied to permit a good electrical contact with the housing so that the sampling electrode will be electrically connected to the housing, which serves as one of its electrical terminals.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a side sectional view of the improved oxygen sensor;

FIG. **2** is an end view of the oxygen sensor of FIG. **1**; and

FIG. **3** is a schematic diagram showing two possible arrangements of an oxygen sensor relative to an engine and a catalytic converter.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. **1**, the improved oxygen sensor, shown generally at **10**, has a tubular metal housing **12** welded to body member **14** by weld bead **16**. Pipe threads **18** on the outside of body member **14** permit the sensor to be threaded into the side of a member in the exhaust path of an engine in the same manner as a spark plug.

A wafer of solid electrolyte material **22**, which will generate an electrical voltage in response to a difference in the partial pressures of oxygen contacting its sampling surface **24** and its reference surface **26**, is mounted and hermetically sealed in a recess **28** in the end **30** of the housing **12**. Although the recess **28** is shown as being formed by an outwardly extending flanged portion **32** of the housing, the recess could also be formed in the end of a cylindrical tube by decreasing the tube wall thickness by removing a portion of the internal wall.

Since the oxygen sensor **10** must withstand the rugged, changing environment of an automotive exhaust system, it is essential that the electrolyte wafer **22** be able to remain stable, non-porous and in hermetically sealed contact with the metal housing **12** for long periods of time. We have found that a durable hermetic seal is possible when a particular combination of materials and structural configurations are used in the manufacture of the improved sensor. A housing made of Series **409** stainless steel has been found to provide the degree of oxidation resistance required and to provide a durable hermetic seal with a MgO stabilized zirconia wafer when the housing and wafer are joined to each other by a layer **36** of the previously identified metal oxide frit containing CrO_3, TiO_2 and SiO_2. The frit should have the property of wetting both the surface of the zirconia wafer and the pre-oxidized stainless steel housing. It should also be of a non-electrically conductive material which is non-reactive with the exhaust gases and also non-reactive with the electrodes. The melting point of the frit should be below that of the stainless and above that of the engine exhaust gases, e.g., in the range of 1700° – 2200°F. Preferably, the radial space between the wafer and housing is maintained to a close tolerance such as 0.003 inch. The previously identified MgO stabilized zirconia composition No. 1027 has been found to offer superior thermal shock resistance compared to zirconia compositions stabilized with Y_2O_3 or CaO, for example. The electrical properties, however, of MgO stabilized zirconia are slightly inferior. For example, the resistance of a Y_2O_3 stabilized zirconia cell was found to be about an order of magnitude lower than the resistance of the MgO stabilized zirconia cell. Since the resistance of the electrolyte is a function of the degree of stabilization, it is pos-

sible other magnesia concentrations might provide more favorable electrical characteristics, possibly to the detriment of the thermal shock behavior. The **1027** composition gives a combination of electrical and thermal shock characteristics which results in a usable material for the electrolyte.

Although Series **409** stainless steel has good corrosion resistance we have found that it is desirable to make the housing **12** even more corrosion resistant by bonding coatings **38, 40** of the same metal oxide frit used as seal **36** to the outside and inside walls of the housing **12.** The frit coatings **36, 38** and **40** are removed from the end surface **44** of the housing **12** in order to expose the underlying metal for electrical contact by the sampling side electrode **46.** The electrode **46** comprises an annular ring of the aforementioned silver-palladium paste which is fired on at a temperature of about 1700°F. for 15 minutes in air.

The reference side electrode **50** is preferably applied and fired as a circular spot in two steps and is preferably of the same silver-palladium alloy as electrode **46.** After the first layer **50***a* is applied, an electrode lead wire **52** is attached to it by the second layer **50***b* of the electrode. The lead wire **52** is preferably spot welded at **54** to an inner metal tubing ferrule **56.** The tubular member **56** comprises a rigid terminal to which electrical connections may readily be made, thus protecting the delicate lead wire **52.** The tubular ferrule **56** is electrically insulated from the body member **14** by an alumina insulator sleeve **58.** The sleeve **58** is affixed to the body **14** and the ferrule **56** by an electrically insulating ceramic cement **60,** such as that sold by Sauereisen Cements Co., Pittsburgh, Pa., under the name of Electrotemp Cement No. 8.

The dimensions of the various elements comprising sensor **10** are preferably selected to maximize the ability of the device to instantly respond to changes in the oxygen concentration of exhaust gases being sensed so that the fuel and/or air input **62** to an engine **64** (FIG. **3**) can be automatically and continually adjusted by an air/fuel ratio controller **66** connected between the oxygen sensor **10** and the engine input **62.** In FIG. **3,** the sensor **10** is shown in its preferred position in full lines downstream of an engine **64** but it could also be positioned immediately downstream of the converter **70** as shown in dotted lines at **10'**, although such position would cause it to be brought to operating temperature more slowly.

We claim:

1. An oxygen sensor adapted for use in an automotive exhaust stream wherein it must be repeatedly subjected to rapidly changing temperatures from ambient to as high as 1700°F. comprising a corrosion resistant tubular metal housing portion; coupling means on a body portion integral with the housing portion for mounting the sensor to complementary coupling means in the engine exhaust path so that the exterior surface of the housing portion can be positioned in the said exhaust path to be contacted by the exhaust stream and the internal surface of the housing portion can be contacted by a reference oxygen source; a wafer of oxygen sensitive solid electrolyte material positioned in a plane at right angles to the axis of the tubular housing portion, said wafer being mounted in a recess in said one end of the housing portion so as to be mechanically restrained against inward axial movement by a ledge portion formed in said housing portion, said wafer closing the end of said tubular housing portion and having opposed outer and inner sampling gas and reference gas contacting surfaces; hermetic fastening and sealing means comprising a metal oxide frit fired to said body member at a temperature higher than 1700°F after said body member has been pre-oxidized, and to said wafer; said sealing means, said tubular metal housing portion, and said wafer having thermal expansion characteristics which are sufficiently close to permit said hermetic seal to remain intact through a temperature range of at least −30°F to **1700°F** when said wafer and housing are positioned in close proximity to each other; a pair of electrodes bonded to the sampling surface and to the reference surface of said wafer; means for electrically connecting one of said pair of electrodes to said body member; means including a lead wire portion connected to the other of said pair of electrodes and passing through the reference end of said body member for permitting an electrical connection to be made remotely from said wafer; a sleeve-like insulation member positioned internally of said body member at the reference end thereof for preventing electrical contact between said last named means and said body member, and aperture means at the reference end of said body member for permitting a reference oxygen source to communicate with the reference surface of said wafer.

2. An oxygen sensor in accordance with claim **1** wherein each of said pair of electrodes covers only a portion of the surface of the wafer.

3. An oxygen sensor in accordance with claim **2** wherein said pair of electrodes comprise an Ag-Pd alloy bonded to the wafer.

4. An oxygen sensor in accordance with claim **1** wherein said means which includes a lead wire portion further includes a hollow metal tube to which said lead wire portion is welded internally of said body member, said hollow metal tube extending through and beyond said insulation member so as to provide a rigid, external electrical connection point.

5. An oxygen sensor in accordance with claim **4** wherein said insulation member is bonded to said body member and to said hollow metal tube by a high temperature electrically insulating cement.

6. An oxygen sensor in accordance with claim **1** wherein said wafer comprises ZrO_2 stabilized with MgO.

7. An oxygen sensor in accordance with claim **1** wherein said frit comprises a mixture of CrO_3, TiO_2 and SiO_2.

8. An oxygen sensor in accordance with claim **1** wherein said coupling means comprises a male pipe thread.

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