

[54] APPARATUS FOR MEASURING OXYGEN CONTENT OF A FLUID

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

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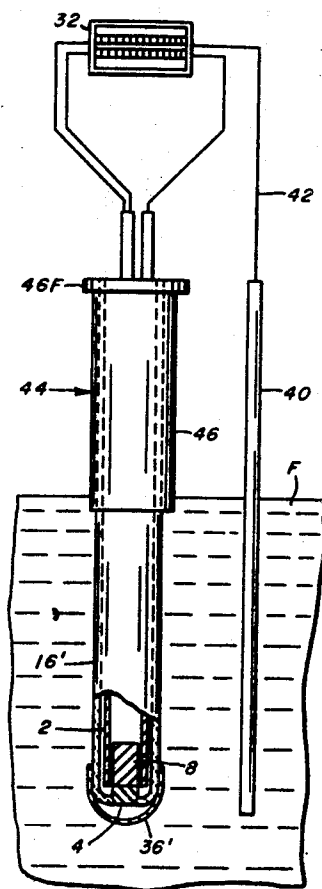
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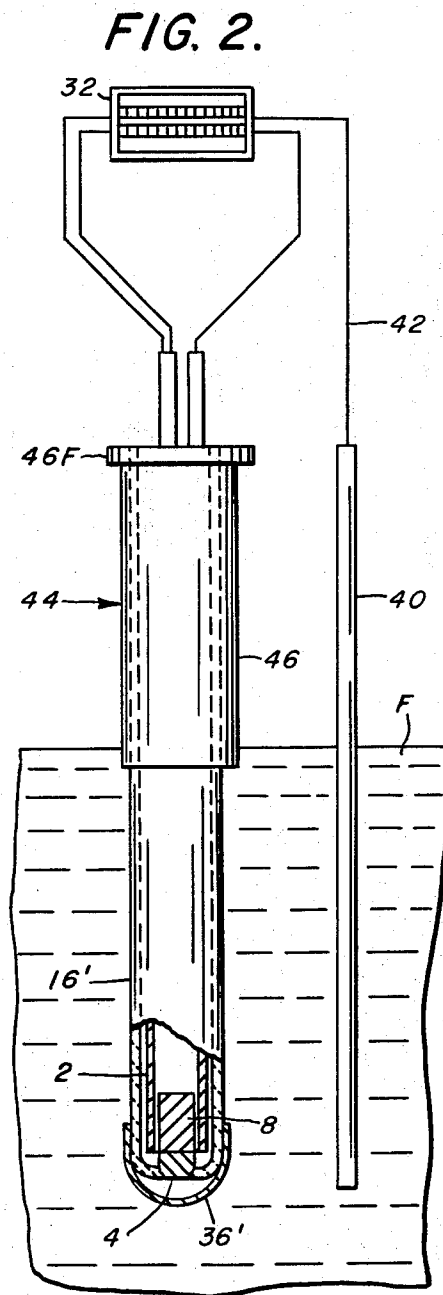
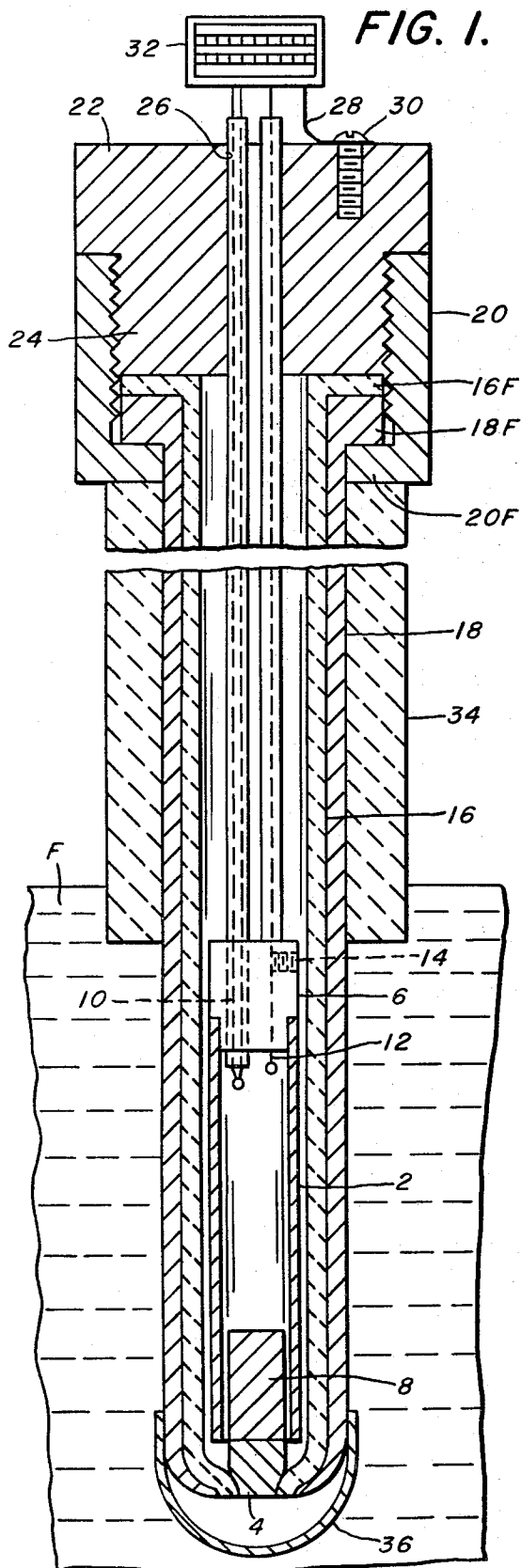
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[57] ABSTRACT

Apparatus for measuring oxygen content of fluids at elevated temperatures includes a sensor or probe which comprises a Cr_2O_3 tube and a solid electrolyte button sealing that end of the tube that contacts the fluid. A solid oxygen reference material in the tube made of chromium or a chromium alloy contacts the button and the other end of the tube is sealed with a molybdenum cap. A thermocouple and a lead wire pass through the cap into the tube. A quartz tube surrounds the Cr_2O_3 tube and button with its outer end in sealing engagement with the button. An electronic conductor has one end extending into the fluid. In one embodiment the conductor is a tube surrounding the quartz tube and in another it is a separate rod or tube. In both embodiments the conductor is preferably a mixture of Al_2O_3 and molybdenum. The lead wire and the other end of the conductor are connected to a voltage measuring means.

12 Claims, 2 Drawing Figures





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APPARATUS FOR MEASURING OXYGEN CONTENT OF A FLUID

This invention relates to apparatus for measuring the oxygen content and/or activity of fluids at elevated temperatures, and more particularly, to apparatus that rapidly determines the oxygen content of liquid steel in a furnace or container without removing a sample. Since our invention, at present, is most useful and most needed for this purpose, this use will be stressed hereinafter. However, our invention is also applicable for determining oxygen in other fluids at temperatures above approximately 700° C., such as oxygen in liquid copper or hot furnace gases.

Apparatus suitable for this purpose is disclosed in the co-pending application of Fruehan and Turkdogan, Ser. No. 39,530, Filed May 21, 1970. However, the apparatus disclosed therein is basically laboratory apparatus and is not suitable for use in large steelmaking furnaces and containers because of cost, fragility, reliability when used by relatively unskilled workmen, ease of use and other factors important in adapting the basic cell concept to industrial use.

Other apparatus suitable for commercial work is disclosed in our co-pending application Ser. No. 54,986, Filed July 15, 1970. The apparatus shown therein is inexpensive, but can only be used once. It is sometimes desirable to have such apparatus that can be re-used even though it is more expensive and it is for this purpose that the present probe was developed.

It is therefore an object of our invention to provide apparatus for measuring oxygen content and temperature in substantially the same theoretical manner as that of our prior application, but which can be re-used.

This and other objects will be more apparent after referring to the following specification and attached drawings, in which:

FIG. 1 is a sectional view of one embodiment of our invention; and

FIG. 2 is an elevation, with parts broken away, and shown in section of another embodiment of our invention.

Referring more particularly to FIG. 1, reference numeral 2 indicates a metallic oxide tube having its lower or outer end sealed by an electrolyte button 4 made of ZrO_2 containing 3 to 10% CaO and its upper or inner end sealed by a molybdenum cap 6. For best operation the size of the button is kept as small as possible. An oxygen reference material 8 is located within tube 2 in contact with button 4. The reference material 8 must be liquid or solid at the operating temperature and is preferably chromium or a chromium alloy such as a Ni-Cr alloy. However, Mo, Ta, or an alloy thereof may be used. The tube 2 must be an oxide of the reference metal, must not melt at the temperature of use, and must act as an electronic conductor at that temperature. The tube is preferably made of Cr_2O_3 . A thermocouple 10 passes through cap 6 with its lower end extending into tube 2. The thermocouple 10 may be of a standard straight type with its two wires passing through a 2-hole refractory insulator, but is preferably a standard U-tube type in which one wire is secured in each leg of the U-tube and connected at the center of the tube. One such thermocouple is shown in Mead U.S. Pat. No. 2,999,121 dated Sept. 5, 1961, or 3,298,874 dated Jan. 17, 1967. A refractory insulated molybdenum wire 12 passes through cap 6 into tube 2 and is held in place by set screw 14. A quartz tube 16 surrounds tube 2 with its lower end in sealing engagement with button 4 which does not extend beyond the end of the tube 16. The tube 16 includes an outwardly extending radial flange 16F at its upper end. For best operation a slight clearance such as 1 mm. should be provided between tubes 2 and 16 to prevent cracking of tube 16 due to thermal expansion. A cermet tube 18 closely surrounds the tube 16 and has its bottom tapered inwardly with an opening therein for exposure of the button 4 to the fluid F being analyzed. The tube 18 has an outwardly extending radial flange 18F at its upper end which abuts flange 16F. The tube 18 must be made of a material which is an electronic conductor and will not melt at the temperature of use. Its metallic phase should be the same as that of cap 6 and wire 12 since otherwise a thermo-electric correction must be made to the electrolytic cell reading. It is preferred to use a mixture

of Al_2O_3 and molybdenum. An internally threaded sleeve 20 surrounds flanges 16F and 18F and has a bottom flange 20F which bears against flange 18F. A cap 22 has a threaded reduced diameter section 24 which is threaded into sleeve 20 to hold the parts assembled. The cap 22 has a hole 26 therethrough for passage of the insulated thermocouple wires and wire 12. A wire 28, preferably made of molybdenum, is attached to cap 22 by means of a screw 30. The sleeve 20 and cap 22 must be electrically conductive and are preferably fabricated from the same metal as the metal phase of the cermet tube 18, but if these parts are at a reasonably uniform temperature in use, no significant thermo-electric error is created if the parts are made of stainless steel. The thermocouple wires and wires 12 and 28 are connected to a potentiometer 32. If the assembled unit is to be placed in a metal bath F with a portion of the cermet tube 18 exposed to slag or to air, a refractory oxide sleeve 34 of a material resistant to slag attack and oxidation is preferably placed over that portion of tube 18 so exposed. Sleeves made of aluminum oxide or magnesium oxide are examples of such protective refractory materials, but this does not exclude other refractory oxides or combinations thereof. In addition, if the sensor is to penetrate a slag layer during immersion, a metal cap 36 is placed over the end of the sensor to protect the electrolyte. This cap must be made of a material which will melt upon contacting the molten metal. In measuring the oxygen content of steel, a steel protective cap is usually employed. To provide a snug fit between button 4 and quartz tube 16 the quartz tube 16 may be heated so that it flows around the electrolyte button 4. Another method is to precision grind the electrolyte button 4 so that it just fits inside the quartz tube 16. In either case, the end of the tube 16 should not extend beyond the electrolyte button and should be ground off, if necessary.

In operation, the sensor can either be partially immersed (about one half of its length) from above the metal bath or installed in the side wall or bottom of a refractory container such as a steel ladle. The molten metal F containing an unknown amount of dissolved oxygen content contacts the exposed end of the zirconia button 4 and also the exposed end of cermet tube 18 which is an electrical conductor. Thus, an electrical connection is made from button 4 through tube 18, sleeve 20, cap 22 and lead 28 to potentiometer 32. An electrical connection is also made from button 4, through the reference alloy 8, oxide tube 2, cap 6 and wire 12 to the other terminal of potentiometer 32. The emf that is read, in combination with the temperature, can be mathematically converted to oxygen content by the general formulas shown in the Fruehan et al. application.

In the embodiment of FIG. 2 a separate rod 40 is used in place of tube 18 and is made of the same material as that tube. One end of the rod 40 is inserted in the fluid F and the other end connected by means of lead 42 to potentiometer 32. Those parts of probe 44 within quartz tube 16' are the same as in the first embodiment of the invention and are indicated by the same reference numerals. Tube 16' differs from tube 16 by the omission of flange 16F. A protective alumina tube 46 surrounds the tube 16' and is cemented thereto by refractory cement. The tube 46 has a radial flange 46F at its inner end. A protective metal cap 36' may be provided over the lower end of tube 16' for the same reason as cap 36 in FIG. 1. This embodiment is less expensive than the first embodiment because the cost of the rod 40 is substantially less than the cost of tube 18. The operation of this embodiment is essentially the same as that of the first embodiment.

While two embodiments of our invention have been shown and described, it will be apparent that other adaptations and modifications may be made without departing from the scope of the following claims.

We claim:

1. Apparatus for measuring the oxygen content of a fluid comprising a first tube, an electrolyte button sealing the outer end of said first tube and adapted to contact said fluid, a metallic oxygen reference material within said first tube in

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contact with said button, said reference material being non-volatile at the operating temperature, said first tube being an oxide of the metal of said oxygen reference material and acting as an electronic conductor at the operating temperature, a thermocouple passing into said first tube and having leads connected to its inner end, a lead wire electrically connected to said first tube, a second tube surrounding said first tube and said button with its outer end in sealing engagement with said button, said leads and lead wire passing through said second tube, a second electronic conductor adapted to contact said fluid, and means connected to said lead wire and said second electronic conductor to measure the voltage flow through said fluid.

2. Apparatus according to claim 1 in which said first tube is made of Cr_2O_3 , said button is made of ZrO_2 containing 3 to 10% CaO , said reference material is of the class consisting of chromium and chromium alloys, and said electronic conductor is a mixture of Al_2O_3 and molybdenum.

3. Apparatus according to claim 2 in which said second electronic conductor is a third tube surrounding said second tube.

4. Apparatus according to claim 3 including a molybdenum cap sealing the upper end of said first tube with said lead wire and thermocouple passing therethrough.

5. Apparatus according to claim 4 including a flange extending radially outward from the inner end of said second tube, a flange extending radially outward from the inner end of said third tube and abutting the flange on said second tube, an internally threaded sleeve surrounding said flanges and

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having a flange engaging the flange on said third tube, a male threaded cap threaded into said sleeve, and a lead extending between said cap and said voltage measuring means.

6. Apparatus according to claim 5 in which said internally threaded sleeve and male threaded cap are stainless steel.

7. Apparatus according to claim 6 including a protective sleeve surrounding a portion of said third tube with one end bearing against the flange of said stainless steel sleeve.

8. Apparatus according to claim 1 in which said second electronic conductor is a third tube surrounding said second tube.

9. Apparatus according to claim 8 including a protective sleeve surrounding said third tube on the inner side of said first tube.

10. Apparatus according to claim 8 including a flange extending radially outward from the inner end of said second tube, a flange extending radially outward from the inner end of said third tube and abutting the flange on said second tube, an internally threaded sleeve surrounding said flanges and having a flange engaging the flange on said third tube, a male threaded cap threaded into said sleeve, and a lead extending between said cap and said voltage measuring means.

11. Apparatus according to claim 1 in which said second electronic conductor is an elongated member spaced from said second tube.

12. Apparatus according to claim 1 including a cap sealing the upper end of said first tube with said lead wire and thermocouple passing therethrough.

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