United States Patent [19]

Handman et al.

[11] **3,864,232**

[45] **Feb. 4, 1975**

[54] **APPARATUS FOR MONITORING THE OXYGEN CONTENT OF HIGH TEMPERATURE FLUIDS**

[75] Inventors: **Lawrence M. Handman,** Cherry Hill, N.J.; **Charles E. Spangler,** Pittsburgh, Pa.; **Raymond F. Thompson,** Bristol, Va.

[73] Assignee: **Westinghouse Electric Corporation,** Pittsburgh, Pa.

[22] Filed: **May 2, 1973**

[21] Appl. No.: **356,669**

[52] **U.S. Cl.** .... **204/195 S**
[51] **Int. Cl.** **G01n 27/30,** G01n 27/46
[58] **Field of Search** .... 204/195 S, 1 T; 324/29

[56] **References Cited**

UNITED STATES PATENTS

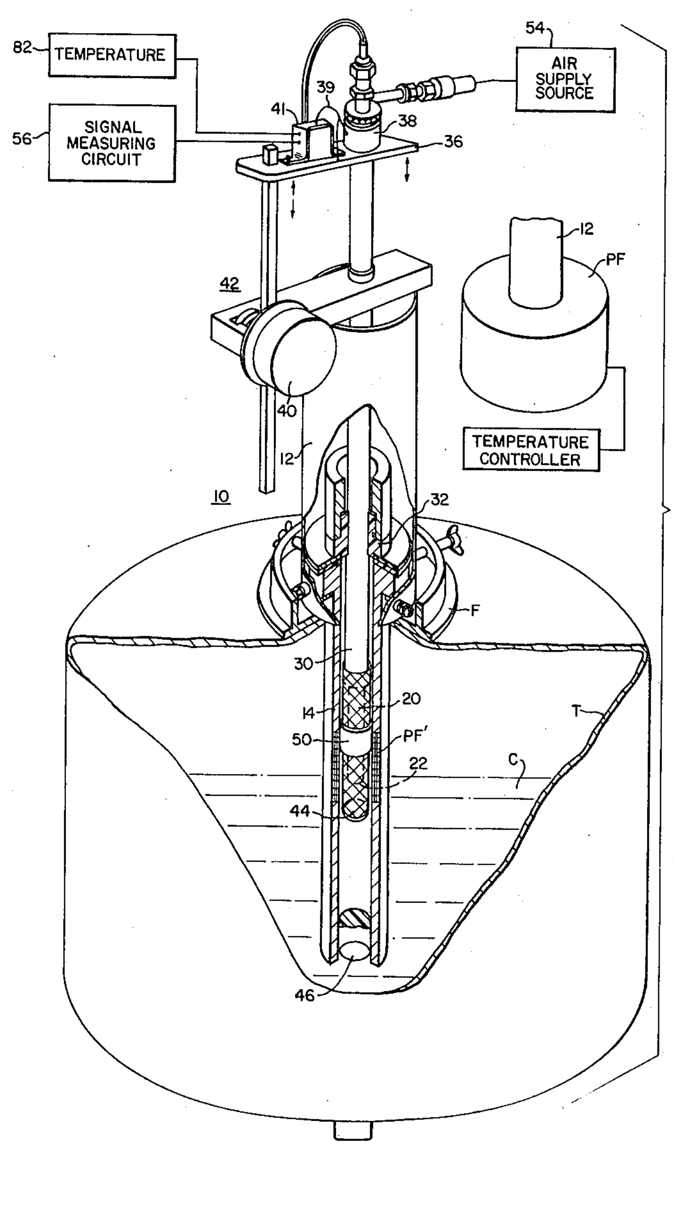
3,619,381	11/1971	Fitterer	204/1 T
3,652,427	3/1972	Flood et al.	204/1 T
3,719,574	3/1973	Richardson	204/195 S

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—M. P. Lynch

[57] **ABSTRACT**

A probe assembly including an oxygen ion conductive solid electrolyte electrochemical cell is preheated under controlled conditions to a temperature equivalent to the temperature of a high temperature oxygen containing fluid such as a gas or molten metal prior to insertion of the probe into the fluid for measuring the oxygen concentration of the fluid. The preheating of the solid electrolyte electro-chemical cell coupled with the use of thermal shield elements within the probe assembly prevents physical deterioration of the solid electrolyte electrochemical cell due to the thermal shock produced when contacting the high temperature fluid.

1 Claim, 4 Drawing Figures



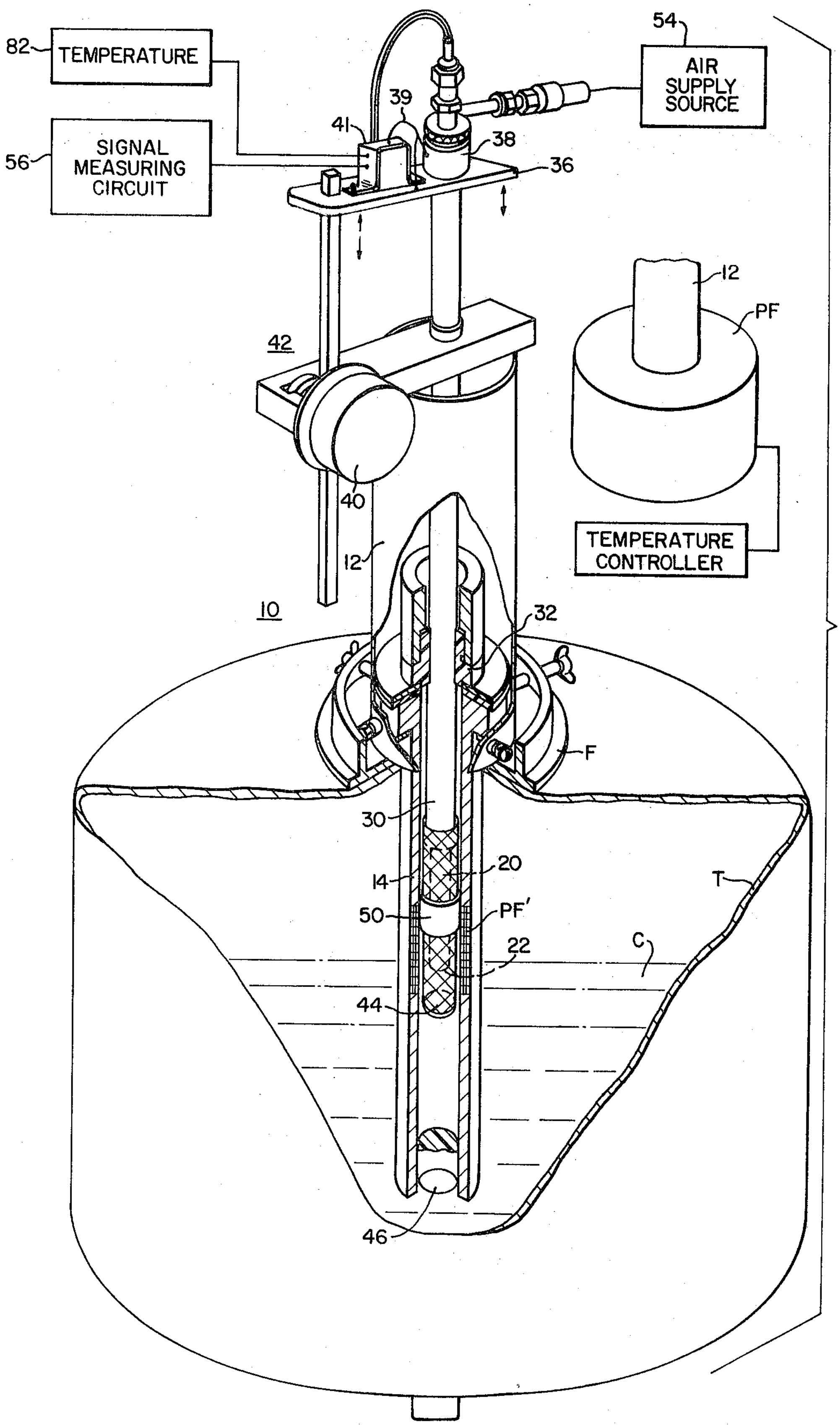

82
TEMPERATURE
56
SIGNAL MEASURING CIRCUIT
54
AIR SUPPLY SOURCE
39
41
38
36
42
12
PF
40
TEMPERATURE CONTROLLER
10
32
F
30
20
14
T
50
PF'
22
C
44
46

FIG. I.

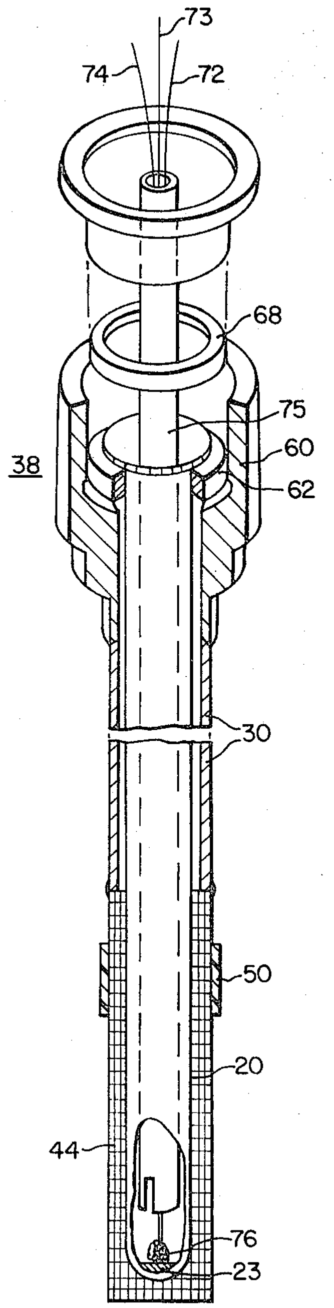


FIG. 2.

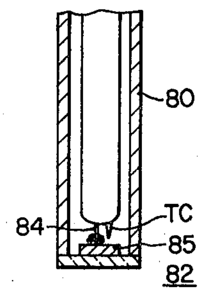


FIG. 3.

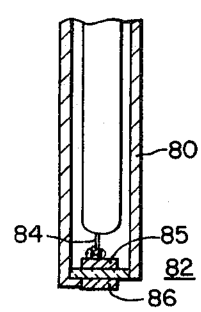


FIG. 4.

APPARATUS FOR MONITORING THE OXYGEN CONTENT OF HIGH TEMPERATURE FLUIDS

BACKGROUND OF THE INVENTION

The measurement of the oxygen content of various fluids used in industrial processes is often a very important parameter. For example the oxygen concentration of molten copper, prior to casting is a key process parameter in continuous melting, casting and rolling operations. A high concentration of oxygen in molten metal results in frequent breaks of the billet and loss of production due to excessive gas evolution in the billet during solidification. A low concentration of oxygen also results in loss of production due to lower strength of the hot billet. Excessive fluctuation of oxygen beyond specification limits adversely affects the quality of the metal product thereby seriously affecting the marketability of the product.

At present, the oxygen content of molten copper is controlled by blowing either a reducing gas or an oxidizing gas stream on the copper as it flows from the holding furnace tothe tundish. If the oxygen content is low, air is blown into the copper. High oxygen is corrected by blowing the hydrogen rich gas stream into the copper. Tundish samples taken periodically are removed and analyzed in a remote laboratory. During the 5 to 10 minute period required to sample and analyze the molten metal an additional 2,500 to 5,000 pounds of copper can be cast at the typical rate of 15 tons/hour. There exists an urgent need for an in situ oxygen measuring technique which will not only provide an accurate oxygen content measurement of high temperature fluids but which will eliminate the time consuming practice of removing samples for analysis in a remote laboratory.

While the conventional solid electrolyte oxygen analyzers offers a rapid direct measurement of oxygen, such analyzers have not been successful in applications requiring continuous measurement of oxygen in high temperature industrial processes. The main disadvantage results from the fact that material compositions of the solid electrolyte at room temperature generally cannot withstand the thermal shock encountered when contacting a high temperature fluid such as a molten metal at 700°C or higher.

SUMMARY OF THE INVENTION

An improved technique and apparatus for monitoring the oxygen content of high temperature environments including gases and/or liquids is disclosed herein.

The traditional fully stabilized solid electrolyte is replaced with a partially stabilized solid electolyte to improve the physical characteristics of the electrolyte to enable it to better withstand elevated temperatures.

The solid electrolyte electrochemical cell is incorporated into a probe assembly and is controllably preheated to a temperature representative of the fluid to be monitored for oxygen content. The preheating of the solid electrolyte electrochemical cell prior to insertion into the fluid eliminates the occurrence of thermal shock when the cell contacts the fluid thus avoiding physical deterioration of the cell.

The specific embodiment of the invention described below with reference tothe accompanying drawings refers to an oxygen ion conductive solid electrolyte electrochemical cell which is controllably preheated to the temperature of the molten metal under consideration and subsequently positioned within a thermal insulating tubular member for insertion directly into the molten metal. The thermal insulating tubular member is a part of a probe assembly capable of being mounted directly on the tundish within which the molten metal is contained. A vertical positioning mechanism associated with the probe assembly functions to lower the solid electrolyte electrochemical cell assembly through the tubular insulating member and into the molten metal for direct contact measurement of the oxygen concentration in the molten metal. Suitable thermal insulating devices within the probe assembly permit subsequent retraction of the solid electrolyte electrochemical cell to a position within the tubular thermal shield member and the subsequent removal of the probe assembly from the tundissh.

DESCRIPTION OF THE DRAWINGS

The invention will become more readily apparent from the following exemplary description in connection with the accompanying drawings:

FIG. 1 is a sectioned illustration of a probe assembly embodying the invention;

FIG. 2 is a detailed sectioned illustration of the solid electrolyte electrochemical cell assembly of the probe assembly of FIG. 1;

FIG. 3 is a schematic illustration of an alternate configuration of the solid electrolyte electrochemical cell assembly for use in the probe assembly of FIG. 1; and

FIG. 4 is a modification of the configuration of FIG. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1 there is illustrated an oxygen probe assembly **10** inserted through a flange member F in the top of a tundish T containing molten copper C. The oxygen measuring probe assembly is supported on the flange F by tubular housing **12.** Extending from the tubular housing **12** into the tundish T and contacting molten copper C is an open ended tubular thermal shield **14** composed of a thermal insulating material capable of withstanding the temperature of the molten copper which is typically in the range of 2,000° to 2,500°F. A clay-graphite composition has proven to be most suitable for fabrication of the tubular shield **14.** The tubular solid electrolyte member **20** having a closed end forming an electrochemical cell **22** extends through the tubular stainless steel member **30** to connector assembly **38** which is secured to mounting plate **36.** The tubular stainless steel member **30** extends from the connector assembly **38** through the stuffing gland **32.**

The vertical position of the mounting plate **36** and consequently the vertical position of the combination of the solid electrolyte electrochemical cell **22,** which as seen in FIG. **2,** is comprised of the solid electrolyte material forming the closed end of the electrolyte member **20** and the electrode **23,** and the tubular stainless steel member **30** is controlled by knob **40** and gear train **42.**

Extending from the tubular stainless steel member **30** is a closed end tubular screen member **44** which surrounds the solid electrolyte member **20** and the electrochemical cell **22.** The tubular screen member functions to:

1. dislogdge the thermal plug element **46** prior to the insertion of the electrochemical cell **22** into the molten copper,
2. prevent damaging contact between the fragile solid electrolyte member **20** and the thermal shield **14**,
3. provide controlled contact between the electrochemical cell **22** and the molten copper by shielding the cell **22** from sudden splashes of molten metal during the time after the plug **46** is dislodged and before the cell **22** is submerged in the molten copper.

A collar of thermal insulating material **50** is secured to the tubular screen member **44** and moves vertically within the tubular shield member **14** to maintain alignment of the solid electrolyte member **20** within the thermal shield **14**. The thermal plug element **46** serves to prevent hot metal and gases from rising within the probe assembly **10** before insertion of the electrochemical cell **22** into the molten metal.

The solid electrolyte electrochemical cell **22** corresponds essentially in method of operation to the solid electrolyte oxygen analyzer described in U.S. Pat. No. 3,400,054, issued Sept. 3, 1968 and assigned tothe assignee of the present invention. An oxygen reference of known oxygen concentration is established within the solid electrolyte member **20** at the closed end by an air supply source **54**. When brought in contact with the molten copper C, the solid electrolyte electrochemical cell assembly transmits an EMF signal to signal measuring circuit **56**. The magnitude of EMF signal is a function of the difference in oxygen partial pressure between the oxygen reference established by the air supply and the oxygen concentration of the molten copper C. The EMF signal is an indication of the oxygen concentration of the molten copper C.

Prior to positioning the probe assembly **10** on flange F, the probe assembly **10** is positioned on preheat furnace PF such that the thermal shield **14** and solid electrolyte member **20** are inserted within the furnace PF. The electrochemical cell **22** is subjected to a controlled heating process by temperature controller TC to preheat the electrochemical cell **22** to a temperature equal to or exceeding the temperature of the molten copper. The gradual heating of the electrochemical cell **22** by the preheat furnace PF establishes the cell **22** at the temperature of the molten copper without subjecting the cell **22** to a thermal shock which could be detrimental to the physical integrity of the solid electrolyte material. Once the temperature of the electrochemical cell **22** has been established at the temperature of the molten copper C by the preheat furncae PF the oxygen probe assembly **10** is ready to be transferred to the tundish T. During the transfer process and prior to insertion of the oxygen probe assembly **10** into the flange F the tubular thermal shield member **14** and the thermal plug element **46** function to minimize heat loss from the solid electrolyte electrochemical assembly **20** to the enviroment.

After the oxygen probe assembly **10** has been heated to the desired temperature by the preheat furnace PF the assembly is installed on the tundish T with the bottom of the tubular housing **12** position in the flange F. With the assembly **10** in position on the tundish T, the tubular thermal shield member **14** extends inside the tundish T through the gas burner flame to a position below the molten copper level.

When the oxygen concentration measurements of the molten copper are desired, the combination of the solid electrolyte member **20** and the tubular stainless steel member **30** are lowered through the thermal shield member **14** by the adjustment of knob **40**. The closed end tubular metallic screen member **44** dislodges the thermal plug element **46**, which then assumes a floating position on the surface of the molten copper and is subsequently removed as part of the slag. The tubular metallic screen member **44** contacts the molten copper and functions as an electrical ground through the stainless steel tube **30** to the electrical connector **41** mounted on the mounting plate **36**. The molten coppr C contacting the electrochemical cell **22** upon immersion into the molten copper serves to provide an external electrode on the external surface of the solid electrolyte member **22** in opposed relationship with the electrode **23**. The molten copper thus completes the ingredients required to form an operational solid electrolyte electrochemical cell as defined in the above reference U.S. Patent and the electrochemical cell **22** immediately functions to produce an EMF signal which is measured by the signal measuring circuit **56** as indication of the oxygen concentration of the molten copper.

The stuffing gland **32**, which provides a slidable seal for the vertical movement of the tubular stainless steel member **30**, also functions to reduce the natural convection inside the tubular thermal shield member **14** thus minimizing heat losses while also preventing tundish burner flames from rising up through the probe assembly **10**.

The requirement for removing the probe assembly **10** for preheating in a remote preheater furnace PF can be eliminated by incorporating a preheating furnace PF' as part of the probe assembly **10** of FIG. **1**. The incorporation of a tubular preheating furnace within the tubular thermal shield element **14** coupled with a temperature control circuit can provide direct heating of the electrochemical cell **22** while the probe assembly **10** is positioned in the tundish T.

Referring to FIG. **2** there is illustrated the solid electrolyte electrochemical cell **22** as including the closed end of the oxygen ion conductive solid electrolyte member **20** and the electrode **23** disposed on the inner surface of the closed end to serve as the oxygen reference electrode in response to the air flow introduced into the interior of the solid electrolyte member **20** by the air supply source **54**. The essential requirement for the material composition of the solid electrolyte material is that it support substantial oxygen ion conductivity while withstanding relatively high temperatures. While this material requirement can be satisfied by the numberous fully stabilized compositions described in the above-referenced U.S. Patent, such as the calcium stabilized zirconia composition represented as $ZrO_2 \cdot$ 15 mol percent CaO, experimental analysis indicates that partially stabilized electrolyte compositions offer additional advantages. The partial stabilization in contrast to complete stabilization provides for improved physical strength and is therefore desirable for the relatively severe environmental operating conditions to which the solid electrolyte material of a molten metal sensor is subjected. A particularly useful partially stabilized calcia-zirconia electrolyte composition is represented as $ZrO_2 \cdot$ 3.5 mol percent CaO.

The conical top of the solid electrolyte member **20** sits inside connector **60**, to which the tubular stainless steel member **30** is affixed. Washer **62** is made of a high temperature insulating material and serves as a cushion for the solid electrolyte member **20**. Reference oxygen from the oxygen supply **54** enters the solid electrolyte member **20** through the connector **70** which mates with connector **60**. Washer **68** provides a mechanical cushion between the connector **70** and the solid electrolyte member **20**.

Electrical continuity between the electrode **23** and the connector **41** mounted on the mounting plate is provided by electrical lead members **72** and **73** which extend through longitudinal passages in a tubular feed through member **75** inserted within the solid electrolyte member **20** to which is attached a metallic mesh electrode **76** which is maintained in intimate contact with electrode **23**. The metallic mesh electrode **76**, which can be typically fabricated from platinum wire mesh, provides positive electrical contact with the electrode **23** while also isolating the solid electrolyte member **22** from direct mechanical contact by the tubular feed-through member **75**.

In addition to being a function of oxygen differential pressure, the EMF signal developed by the electrochemical cell **22** is also responsive to variations in temperature. Therefore in an effort to maintain the temperature of the cell **22** at a third wire **74**, known value having material composition different from the electrical leads **72** and **73**, is passed through another passage in the feedthrough tube **75** to contact the metallic mesh electrode **76** thus forming a thermocouple combination with the electrical leads **72** and **73**. A particular useful thermocouple for monitoring temperatures in the range of molten copper is formed by using platinum for the electrical lead wires **72** and **73** and a platinum **10** percent rhodium material for wire **74**. The thermocouple signal produced is transmitted through the electrical connector **41** to a temperature monitoring circuit **82** illustrated in FIG. **1**.

An alternate solid electrolyte electrochemical cell assembly is illustrated in FIG. **3**. The tubular electrolyte member **20** of FIG. **1** has been replaced by a tubular stainless steel member **80** which supports a dish shape solid electrolyte electrochemical cell **82**. The stainless steel tubular member **80** functions as an electrical lead when in contact with the molten metal and functions in combination with the electrical lead **84** which contacts the inner electrode **85** to transmit the EMF signal developed by the cell **82** to a suitable monitoring circuit.

The configuration of FIG. **3** can be modified as shown in FIG. **4** to monitor high temperature gas environments by adding an external electrode **86** for contacting the gas enviroment and extending the stainless steel tube **80** to contact the electrode **86** and thus functions as an electrical lead wire from the electrode **86**.

We claim:

1. Apparatus for monitoring the oxygen content of molten metal comprising, an open ended tubular member, a solid electrolyte electrochemical cell cell means including an oxygen ion conductive solid electrolyte having an external surface and an internal surface, an electrode means disposed in intimate contact with said internal surface and a reference medium of known oxygen content in contact with said internal surface, said solid electrolyte electrochemical cell means being slidably positioned within said tubular member, said tubular thermal insulating member being adapted for positioning relative to said molten metal, adjustment means for slidably positioning said solid electrolyte electrochemical cell means to project said solid electrolyte electrochemical cell means through the open end of said tubular thermal insulating member to establish said external surface of said solid electrolyte in direct contact with said molten metal and to retract said solid electrolyte electrochemical cell means within said tubular thermal insulating member, said solid electrolyte electrochemical cell developing a signal indicative of the oxygen content of said molten metal, and electrical heater means located within said tubular thermal insulating member at a position adjacent to said solid electrolyte electrochemical cell means to maintain the temperature of said solid electrolyte electrochemical cell at a temperature comparable to that of the molten metal prior to insertion of said solid electrolyte electrochemical cell into said molten metal.

* * * * *