United States Patent [19]

Faurschou et al.

[11] **3,904,486**

[45] **Sept. 9, 1975**

[54] **OXYGEN PROBE WITH SELF-CONTAINED SOURCE OF OXYGEN GAS, METHOD OF USE AND OXYGEN GENERATING COMPOSITION THEREFOR**

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[22] Filed: **July 11, 1974**

[21] Appl. No.: **487,443**

[30] **Foreign Application Priority Data**

July 18, 1973 Canada 176706

[52] **U.S. Cl.** ..... **204/1 T;** 204/195 S; 252/186; 324/29

[51] **Int. Cl.** **G01n 27/46;** C01b 13/08

[58] **Field of Search** ..... 204/195 S, 1 T; 324/29; 252/186

[56] **References Cited**

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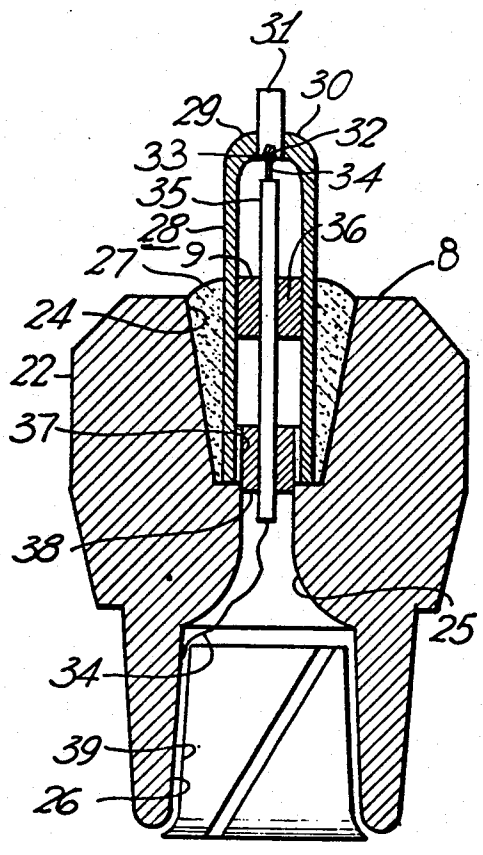
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[57] **ABSTRACT**

An improvement is provided in a probe of the type including a cell disposed in a Vycor cell tube, and having a metal wire connected thereto. The probe, in use, is provided with gaseous oxygen as the reference gas so that it may be used for directly determining the amount of free oxygen gas in molten metal. The improvement involves providing a self-contained solid oxygen-gas source and a vent tube within the Vycor tube. The self-contained solid oxygen-gas source may be a Group II A metal peroxide, e.g., barium peroxide, which decomposes at the operating temperature of the probe to generate substantially pure gaseous oxygen at a pressure of one atmosphere or more while leaving a residue having substantially no vapor pressure at that temperature. The solid oxygen-gas source decomposes at the operating temperature of the probe to bathe the cell with continuously flowing reference oxygen gas. The vent tube is disposed with one open end near the cell and with the other open end outside the cell tube. The vent tube ensures that oxygen which is produced is at a pressure of one atmosphere, and that the oxygen gas replaces any other gas, e.g. air which is in the cell tube.

10 Claims, 2 Drawing Figures



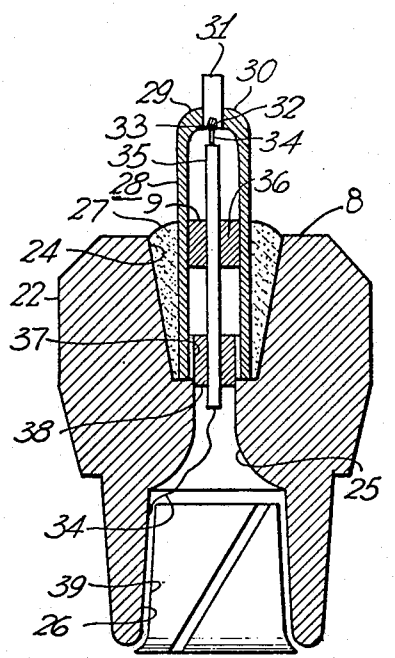

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Fig-1

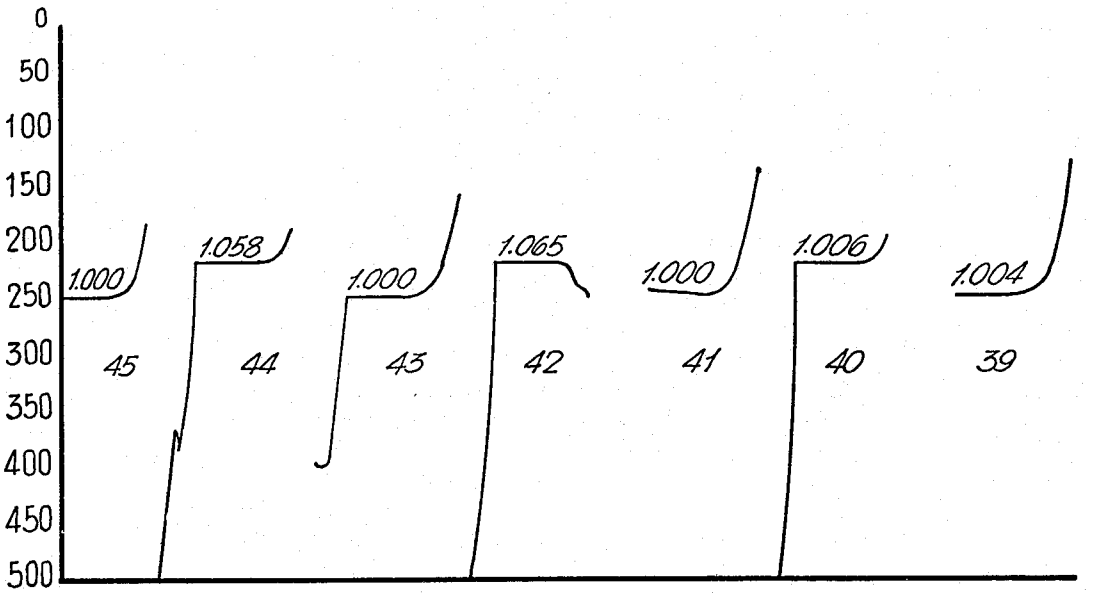

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Fig-2

OXYGEN PROBE WITH SELF-CONTAINED SOURCE OF OXYGEN GAS, METHOD OF USE AND OXYGEN GENERATING COMPOSITION THEREFOR

FIELD OF THE INVENTION

1. General Nature

This invention relates to an improvement in a probe for the direct determination of a gas, dissolved in a molten metal. It is more particularly directed to such improvements in a probe for the direct determination of oxygen dissolved in molten steel.

2. The Prior Art

Selective oxidation and subsequent deoxidation form the basis of many commercially important extraction metallurgy processes. Consequently, the determination of the oxygen content of molten metals, for example, iron, iron alloys, steel, nickel, nickel alloys, copper, or copper alloys, has received considerable attention. Methods heretofore used for such oxygen determination were based on the doubtful hope that samples taken from the melt, then solidified and subsequently analyzed would be representative of conditions in the melt. The results which were obtained gave the total amount of oxygen and required several minutes for the analysis in a laboratory adjacent to the area from where the melt sample was taken.

In recent years, the art has provided apparatus for determining the content of the soluble or dissolved oxygen in molten metals by making use of the principles of galvanic oxygen concentration fuel cells. Such measurements have generally been by the use of half-cells which involve the presence of a gas on the reference side of the electrolyte and the gas which is dissolved in the molten metal on the other side of the electrolyte. Examples of such half-cells include: an electrolyte embedded in a ceramic sleeve surrounding the covering surface of the electrolyte; an immersible, hollow, stabilized zirconia cylinder, closed at the immersion end, using air as the reference electrode; such a cylinder including the covering of the enclosed, hollow cylinder of gas impermeable-zirconia, on both the inside and the outside, with gas-permeable zirconia; a fused silica tube with a stabilized zirconia disc tip as the solid electrolyte, sheathed by a sleeve sheath of graphite, and protected from contact with the slag by means of a metal disc; and a pre-cast plug of the electrolyte located in a temperature-resistant non-conducting carrier tube so as to project from, and outwardly seal, the carrier tube.

In all the examples noted above, there was the problem of sensitivity to thermal shock which caused cracking of the electrolyte. In addition, other problems included: the high cost of zirconia tubes; the preheating or slow heating of the electrolyte which introduced a time delay, and thus rendering the zirconia tube suitable for research purposes but not for, e.g., steel mills, since it could not be used in a direct test; the difficulty of fusing the preformed zirconia disc into the quartz tube; and the difficulty in maintaining adequate contact of the electrical lead or leads with the electrolyte. It was thought that thermal shock could be avoided by reducing the mass of the electrolyte, but this has not been found to be universally effective.

An improved form of electrolyte for such probe found to reduce thermal shock was provided in Canadian Pat. No. 895,537 issued Mar. 14, 1972 to Faurschou, et al. The electrolyte was provided in the form of compacts sufficiently impervious to transport of molecular oxygen and of controlled density, e.g., at least about 75% relative density. However, the necessity for providing a continuous source of air as a reference gas involved the use of awkward flexible tubes, conduit connections, meters, etc., which complicated the structure of the probe needlessly.

One suggestion for obviating the necessity for providing a continuous source of air was provided in Canadian Pat. No. 815,672 issued June 17, 1969 to M. Olette and C. Gatellier. In that patent, the reference substance itself contained oxygen whose partial pressure at various temperatures was known. Examples included a mixture of an oxide with a metal or one or more oxides, for example, a mixture of Ta and Ta_2O_5. However, the use of such probe brought about other problems not inherent in the use of a probe having a gaseous oxygen reference.

Another suggestion for obviating the necessity for providing a continuous source of air was provided by Canadian Pat. No. 911,530 issued Oct. 3, 1972 to G. R. Fitterer, who disclosed the use of CO_2 gas. At the elevated temperatures to which the probe is usually subjected, the carbon dioxide dissociated into gaseous oxygen, to provide a reference gas which was a mixture of undissociated carbon dioxide, as well as the dissociated products, carbon monoxide and oxygen. This mixture of gases having different molecular weights, led to an undesirable thermal diffusion effect, in which heavier gases tended to concentrate at the colder areas. Since the emf generated using carbon dioxide as the reference gas was dependent on the temperature, a very accurate measurement of the temperature had to be made simultaneously with the emf measurement. Thus, because of inherent advantages of the use of gaseous oxygen reference gas, namely, lack of dependence on temperature, it would still be desirable to provide a built-in source of oxygen gas.

AIMS OF THE INVENTION

An object, then, of a principal aspect of this invention is to provide an improvement in the probe to provide a probe tip which contains a source of gaseous oxygen reference gas which gas is released at the operating temperature of the probe.

SUMMARY OF THE INVENTION

Broad Statement of the Invention

By one broad aspect of this invention, an improved probe tip sub-assembly for a probe for the direct determination of a dissolved gas in a molten metal is now provided. It includes the following now conventional elements, namely: a heat-resistant, substantially electrically non-conductive cell tube; a cell, comprising a preformed solid electrolyte compact which retains its ionic conduction properties and which does not exhibit substantial electronic conduction properties at the temperature of the molten metal, secured at one open end of the cell tube; and at least one electrically conductive metallic element in intimate electrical contact with the cell. The improvement comprises disposing within the cell tube, a mass of a source of oxygen gas, which oxygen reference gas is generated at the operating temperature of the probe, while leaving a residue having no substantial vapor phase at the operating temperature of the probe and a vent tube disposed with one open end near the cell, and with the other open end outside the

cell tube. The vent tube ensures that oxygen which is produced is at a pressure of one atmosphere, and that the oxygen gas replaces any other gas, e.g., air which is in the cell tube.

VARIANTS OF THE INVENTION

Structurally, the mass of the source of oxygen gas is preferably provided as a preformed hollow cylinder made from the selected oxygen-releasing material, the cylinder being preferably disposed around the vent tube. As noted above, the vent tube is disposed with one open end adjacent the preformed solid electrolyte cell, the vent tube extending outwardly from, and being secured within, the aft end of the cell tube.

The solid source of oxygen gas is any Group II A metal peroxide (e.g., a peroxide of berylium, magnesium, calcium, or barium) which decomposes at the operating temperature of the probe to generate substantially pure gaseous oxygen at a pressure of one atmosphere or more while leaving a residue having substantially no vapor pressures at that temperature. The solid source which is preferred is barium peroxide. The barium peroxide, when subjected to heat, experiences substantially no oxygen evolution at temperatures below about 500°C. However, the rate of decomposition increases with increasing temperature, reaching a maximum at a temperature of about 850°C. The reaction is substantially completed at about 925°C. The residue (barium oxide) has no substantial vapor phase at the operating temperature of the probe.

Barium peroxide powder is difficult to press together to form a manageable compact. It is therefore necessary to mix the barium peroxide with a suitable binder in order to enable the barium peroxide to be pressed. A suitable binder is one which is compatible with the barium peroxide and also must not decompose at the operating temperature of the probe to produce any material which would interfere with the operation of the probe. One suitable such binder is sodium silicate, in soluble form, as, e.g., sodium metasilicate, anhydrous (Na_2SiO_3); sodium metasilicate pentahydrate; sodium sesquisilicate ($Na_2Si_2O_7$, anhydrous); sodium orthosilicate ($Na_2SiO_3 \cdot 2NaOH$, or $2Na_2O \cdot SiO_2$ [anhydrous] or $2Na_2O \cdot SiO_2 \cdot Si4H_2O$); and water glass ($Na_2O \cdot 375SiO_2$ to $2Na_2O \cdot SiO_2$ with various proportions of water).

In addition, in order to produce compacted barium peroxide by a press, a suitable lubricant must be included with the barium peroxide and the binder. A suitable lubricant is one which is compatible with the barium peroxide and binder and must not decompose at the operating temperature of the probe to produce any material which would interfere with the operation of the probe. One suitable such lubricant is talc. (Talc is a natural hydrous magnesium silicate of the formulae $Mg_3SiO_{10}(OH)_2$ or $3MgO \cdot 4SiO_2 \cdot H_2O$, other forms of such lubricant include magnesium silicate ($3MgSiO_3 \cdot 5H_2O$ with a ratio of $2MgO: 5SiO_2$) and magnesium trisilicate (not less than about 20% MgO nor 45% SiO_2).

While it is preferred to provide the solid source of generated oxygen as a pressed hollow cylinder of barium peroxide, it is possible to use the solid source in other physical forms. It is essential, however, that when the solid source of oxygen decomposes to form gaseous oxygen, the residue does not come into contact with the surface of the cell around the electrical wire and hence shut off the reference oxygen. This may be done by supporting the solid oxygen source on a suitable carrier. A suitable carrier would be any of the now conventional solid catalyst supports, e.g., high surface area silica, alumina, silica-alumina or zeolites. For example, the barium peroxide could be mixed with the water glass, and then coated onto the carrier and then be dried. The product so formed could be suitably placed within the heat-resistant, substantially electrically non-conductive cell tube.

However, it is preferred to provide the barium peroxide as a pressed hollow cylinder supported on, or secured to, the vent pipe. Such pressed hollow cylinder may be formed in the following manner:

A predetermined amount of barium peroxide is thoroughly mixed with a measured amount of sodium silicate having a silica-to-alkali weight ratio of about 3.22 and a viscosity of about 180 centipoise. These ingredients are continuously agitated and mixed thoroughly to a damp coarse sand consistency. The mixture is not allowed to set while it is dried. The air drying could be accelerated by oven drying at controlled temperatures. The dried mixture is screened through various mesh screens ranging from about 40 microns to about 420 microns to eliminate extra coarse and extra fine particles. Such particles are unsuitable for the subsequent pressing.

Such mixture is not necessarily capable of becoming pressed into a predetermined sized pressed hollow cylinder without the addition of a dic lubricant. Such die lubricant must be compatible with both the barium peroxide and the binder. One suitable such lubricant is talc, which should be free of abrasive impurities and possibly also be "Air Floated" and suitable for tablet making. The lubricant could be used in amounts up to about 20% by weight, depending on the size and weight of the pressed hollow cylinder.

In one variant of this aspect of this invention, a plug assembly is provided for the probe described above, the plug assembly including the sub-assembly described above, in combination with a plug which is formed of heat-resistant, substantially electrically non-conductive material, the plug having a longitudinally extending passage with the cell tube being disposed and sealed, with such passage.

There is some criticality in the disposition of the probe-tip sub-assembly in the passage in the plug and this is dependent on the location of the solid mass of oxygen-generating material in the cell tube. The preformed solid mass of oxygen-generating material must be so situated that it receives a suitable amount of radiant heat from the melt immediately, but also that it does not receive so much heat that it decomposes substantially completely to release the reference oxygen gas too quickly. For example, if the barium peroxide is in the form of a hollow cylindrical pellet secured to the vent tube, the sub-assembly is secured within the passage of the plug so that the barium peroxide is shielded by the plug mass, i.e., the forward end of the barium peroxide is substantially coextensive with, or slightly behind, the forward end of the plug. If the barium peroxide is situated too far forwardly (towards the solid electrolyte cell), the oxygen is generated for too short a period of time. Consequently, the signal e.m.f. deteriorates rapidly, and may be completely deteriorated before thermal equilibrium is reached. If the barium peroxide is situated too far rearwardly, the oxygen is generated too slowly. Thus, the cell takes an excessively long time for the signal e.m.f. to stabilize.

The various features of Canadian Pat. No. 895,537 which are ancillary to the present invention are incor-

porated herein by reference. Such features include, but are not restricted to, the nature of the solid electrolyte material, the nature of the heat-resistant, substantially electrically non-conductive cell tube, the nature of the electrically conductive metallic element, the procedures for making the electrolyte compact, the nature of the heat-resistant plug material, and the other features associated with the disposable probe and replaceable lance.

By another variant of this invention, a method is provided for providing a continuous supply of gaseous oxygen reference gas during the use of a probe for the direct determination of oxygen in molten steel involving the use of a solid electrolyte and a galvanic oxygen fuel cell principle, the method comprising: providing a preformed compressed mass of barium peroxide within a restricted zone including the solid electrolyte; decomposing the barium peroxide by the heat of the molten metal; and using the gaseous oxygen so-produced firstly to sweep stagnant gas from the zone at the base of the solid electrolyte, and secondly, to bathe the solid electrolyte with such flowing generated oxygen gas.

The probe is designed to be fitted on a probe lance to facilitate insertion into the melt, the probe being secured to the replaceable lance tip by an easily disconnectable mounting preferably in the manner taught in Canadian Pat. No. 895,537. The electrical connection between the lance handle and the readout unit is through a conventional electrical cable.

The vent tube may be made of any suitable inert material. Such a material can be, for example, mullite, Vycor or ceramic. (Vycor is the Trade Mark for a glass made by a process in which an article fabricated by conventional methods is chemically leached to remove substantially all of the ingredients except silica. When fired at high temperatures a transparent glass of high softening point and extremely low expansion coefficient is produced.

Physical properties: Softening point approximately 1,500°C. Temperature limit in service, 900°C. Linear coefficient of expansion per °C, 0.0000008; sp.gr. 2.18; refractive index 1.458. [A similar glass, No. 7910, will transmit over 60% radiation at 254 millimicrons in 2 mm section.]

The barium peroxide preform is disposed around the vent tube and secured thereto by a suitable cement. Any suitable cement may be used. One suitable cement is water glass, used in a small amount.

The heat-resistant substantially electrically non-conductive cell tube is selected from those recited in Canadian Pat. No. 895,537 disclosed above. Preferably, however, it is Vycor.

The solid electrolyte of the cell is selected from those recited in Canadian Pat. No. 895,537 disclosed above. Preferably, however, it is lime-stabilized zirconia.

The preformed cell is preferably made by the pressure compacting and sintering techniques recited in Canadian Pat. No. 895,537 disclosed above.

The metallic element is selected from those recited in Canadian Pat. No. 895,537 disclosed above. Preferably, however, it may be a Pt—Rh alloy wire, of such relative proportions of Pt to Rh as to give a minimal low thermal offset.

The plug is formed of a heat-resistant, substantially electrically, non-conductive material selected from the those recited in Canadian Pat. No. 895,537 disclosed above.

DESCRIPTION OF THE DRAWINGS

Brief Description

In the accompanying drawings,

FIG. **1** is a central longitudinal cross-section of a plug assembly of one aspect of this invention, provided with the probe tip sub-assembly of another aspect of this invention; and

FIG. **2** is a graph of time as abscissa with e.m.f. in millivolts as ordinate of e.m.f. reading with a representative number of cells of the present invention, compared with the cell of Canadian Pat. No. 895,537.

DETAILED DESCRIPTION

As seen in FIG. **1**, the plug assembly includes a probe tip sub-assembly **28** secured with a plug **22.** Plug **22** is formed with three coaxial interconnecting, longitudinally extending passages, namely first frusto-conical passage **24,** second horn-shaped passage **25,** and third cylindrical passage **26.** Secured with first passage **24** by means of refractory cement **27** is the probe tip sub-assembly **28.** Such sub-assembly **28** includes an outer tube **29** formed by Vycor. Vycor tube **29** contains, at its outer end, a constriction **30,** and heat-sealed within constriction **30** is a cell **31** comprising a premolded mass of sintered solid electrolyte. Jammed into a dead-end hole **32** at the inner end of cell **31** by an interference fit is the spherical end **33** of an electrical lead wire **34,** which preferably is a platinum-rhodium alloy.

Disposed within outer tube **29** is a vent tube **35** preferably formed of mullite, Vycor or ceramic. Tube **35** extends from close to the junction of cell **31** and wire **34** to beyond the inner end of outer tube **29.** Disposed around vent tubr **35** at a preselected distance from either end thereof is a hollow preformed cylindrical pellet **36** of the solid oxygen reference gas releasing agent, i.e., of the pressed hollow cylindrical pellet of barium peroxide/water glass/talc, prepared as described specifically hereinabove. The plug **36** is secured to the vent tube **35** by means of refractory cement **37,** and the vent tube **35**/pellet **36** unit is secured within outer tube **29** by a plug **38** of refractory cement.

Wire **34** passes through vent tube **35** and is secured within passage **26** by contact sleeve **39** which is formed of steel.

The preformed cylindrical cell **31** may be made as follows:

A binder, e.g., about 6% polyvinyl alcohol and about ½% die lubricant is mixed with lime-stabilized zirconia powder, initially of −325 mesh. The mixture is spray-dried to change the shape of the granules to spherical. The particles are then sieved to recover and use only those passing a −200 mesh Tyler screen. Those spherical particles are formed into a suitably shaped tablet, having the dead-end hole at one end thereof. It is first heated to drive off the fugitive binder and then is sintered.

It will be seen that the probe tip sub-assembly is secured within hole **24** of plug **22** in such a way that the front face **9** of pellet **36** is approximately coextensive with front face **8** of plug **22.** Thus, when plug **22** is heated the barium peroxide pellet **36** begins decomposing, and the initially formed oxygen sweeps out the stagnant air at the base of cell **31** within tube **29** by way of vent tube **35.** Continued generation of oxygen enables the oxygen to bathe the cell **31**/contact wire **34** junction continuously and be expelled through vent

tube **35**. The usual time for recording readings is about 10 – 15 seconds. The amount of barium peroxide in the pellet **36** is sufficient to provide a generated oxygen supply for about 30 seconds.

In one such system as tested, expendable probes, a tubular steel lance, and electrical leads were provided, along with control circuitry, with the e.m.f. being recorded using a chart recorder. The probes had a tubular steel body coated with suitable refractory material. The tests were carried out in the manner described in Canadian Pat. No. 895,537 to determine the oxygen content of molten steel in a laboratory type induction furnace. The results of the tests are as follows:

Standard Air Ref. (Canadian Pat. No. 895,537)			BaO_2 Ref.		
Test No.	e.m.f.	$[1000(x-\bar{x})]^2$	Test No.	e.m.f.	$[1000(x-\bar{x})]^2$
1	1.012	16	2	1.070	36
3	1.020	144	4	1.078	196
5	1.010	4	6	1.066	4
7	1.020	144	8	1.056	64
9	1.018	100	10	1.065	1
11	1.012	16	12	1.060	16
13	1.012	16	14	1.065	1
15	1.002	36	16	1.062	4
17	(.990)		18	1.060	16
19	1.004	16	20	1.065	1
21	1.000	64	22	1.072	64
23	—		24	1.068	16
25	1.004	16	26	1.060	16
27	1.013	25	28	1.064	0
29	1.002	36	30	1.063	1
31	1.006	4	32	1.072	64
33	1.007	1	34	(1.040)	
35	(.980)		36	1.060	16
37	1.010	9	38	1.060	16
39	1.004	16	40	1.066	4
41	1.000	64	42	1.065	1
43	1.000	64	44	1.058	36
45	1.000	64	46	1.067	9
47	1.008	0	48	1.062	4
49	1.002	36	50	1.060	16
	$\bar{x}$=1.008	σ=6.5 mv.		$\bar{x}$=1.064	σ=5.1 mv

The above tests were carried out to compare the performance of an air reference (using the probe disclosed and claimed in Canadian Pat. No. 895,537 as the reference) with the probes of the present invention (using a pressed barium peroxide pellet as an oxygen generator). The temperature of the test ranged from: 1,600°F. (for tests 1 – 3); 1,585°F. (for tests 4 – 7); 1,592°F. (for tests 8 – 12); 1,605°F. (for tests 13 – 20**1,600**°1600°F. (for tests 21 – 32); and 1,605°F. (for tests 32 – 50). FIG. **2** shows the recorder chart trace for tests 39 – 45.

It is seen that once equilibrium is established, both the standard probes and the probes of this invention gave a substantially constant e.m.f. reading for about 10 seconds. Furthermore, it can be calculated that the e.m.f. developed by an oxygen reference gas is 65 mv greater than that developed by an air reference gas. It is seen that this theoretical difference is approximately met.

In addition, it is noted from the fifty tests in the table, that the average e.m.f. reading for the standard air reference probe is 1.008 with the standard deviation being 6.5 mv. On the other hand, the average e.m.f. reading for the oxygen reference probe of the present invention is 1.064 mv with a standard deviation of 5.1 mv. It is also noted that with both types of probes the readings of e.m.f. were not identical since the furnace used in the test did not maintain a constant O_2 level in the melt.

Other Variants of the Invention

In one production version of the plug assembly of the present invention, the vent tube is a 1/16 O.D. by 1/32 I.D. mullite tube. The Vycor tube is secured to the ceramic plug by means of Hiloset H.160 cement. (Hiloset is the Trade Mark for a superduty bonding mortar which is wet, but is air setting. It has the following additional characteristics:

Refractoriness Classification	Super-Duty. When tested at 2910°F., mortar did not flow from pier joints.
Water Content (Per ASTM C-92)	Shipped Wet 19–20%
Approximate Weight Per Sq.Ft. As applied As A 150" Coating	1⅛ lbs.
Approximate Weight Required To Lay 1000 9" Straight Brick	350–400 lbs.
Packaging	100 and 200-lb. drums

Bond Strength

Modulus of Rupture	
Temperature	Lbs./Sq.In.
220°F.	850–1200
1000°F.	570–900
1500°F.	400–660
2000°F.	450–880
2250°F.	455–1150
2550°F.	850–1250
2732°F.	1725–2015
2910°F.	2795–3290

Chemical Analysis:

SiO_2	49.55%
Al_2O_3	39.72
Fe_2O_3	1.67
TiO_2	1.15
CaO	0.59
MgO	0.23
Alkalies	4.05
Ignition Loss	3.08)

The spacing of the end of the mullite vent tube from the rear face of the sensor cell is a minimum distance of 1/16 in. The position of the barium peroxide pellet from the rear face of the sensor cell is a minimum of 11/32 in. The front face should not extend beyond the face of the cement, but can be up to ⅛ inch behind the cement. The wire lead is Rh/Pt, which is balled and inserted in the sensor cell. A stainless steel clip is inserted in the plug to retain the wire lead.

The barium peroxide pellet sub-assembly is assembled as follows:

The BaO_2 reference is secured to the mullite tube with sodium silicate at each side of the BaO_2. It is allowed to dry, then the assembly is fed over the Rh/Pt wire lead. It is inserted 6 mm. in the Vycor tube and the rear end is cemented. It is allowed to dry. It is inserted in the plug and finally, it is cemented in position as shown.

The following is the sequence of assembly operation:

1. Fuse cell in closed over Vycor tube and inspect.
2. Ball wire lead and insert in cell and Vycor assembly.
3. Assemble BaO_2 reference and vent tube assembly to Vycor and cell assembly.
4. Cement rear end of assembly, and allow to dry.
5. Thread wire through ceramic plug and secure wire with stainless steel clip.
6. Finally cement self-contained reference assembly to ceramic plug and bake.

SUMMARY

Thus, it is seen that the probe of an aspect of the present invention was more reliable and had less scatter than the air reference probe. Accordingly, at the particular oxygen and temperature levels, the probe of an aspect of the present invention is at least as good as the air reference probe.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Consequently, such changes and modifications are properly, equitably and "intended" to be, within the full range of equivalence of the following claims.

We claim:

1. In a probe tip sub-assembly for a probe for the direct determination of a dissolved gas in a molten metal of the type including:

a. a heat-resistant, substantially electrically non-conductive cell tube;

b. a cell, comprising a preformed solid electrolyte compact which retains its ionic conduction properties and which does not exhibit substantial electronic conduction properties at the temperature of the molten metal, secured at one open end of said cell tube; and

c. at least one electrically conductive metallic element in intimate electrical contact with said cell, the improvement which comprises: a solid source of a reference oxygen gas generating agent disposed within tube (a), said solid oxygen gas generating agent comprising a Group II A metal peroxide, which decomposes as it passes through a temperature within the range of about 850°C – 925°C, thereby to generate substantially pure gaseous oxygen at a pressure of one atmosphere or more, said solid being adapted to generate substantially pure reference oxygen gas at the operating temperature of the probe while leaving a residue having substantially no vapor phase at said operating temperature; and a vent tube, one open end of which is adjacent said cell (b), the other open end of which projects beyond the end of the cell tube (a).

2. The improved sub-assembly of claim **1** wherein the solid oxygen gas generating agent is barium peroxide.

3. The improved sub-assembly of claim **2** wherein the barium peroxide is in the form of a preformed compressed pellet derived from an intimate mixture of barium peroxide, aqueous sodium silicate solution and talc.

4. The improved sub-assembly of claim **3** wherein said compressed pellet comprises a hollow cylindrical pellet of said barium peroxide surrounding, and secured to, a peripheral area of said vent tube, adjacent the mid-point of said tube.

5. The improved sub-assembly of claim **4** wherein said vent tube is secured to the cell tube by refractory cement.

6. A plug assembly for a probe for the direct determination of a dissolved gas in a molten metal, comprising the sub-assembly of claim **4** in accordance with a plug, said plug being formed of heat-resistant, substantially electrically non-conductive material, said plug being provided with a longitudinally-extending aperture, and wherein said cell tube (a) is disposed, and sealed, within said longitudinally-extending aperture.

7. A method of providing a continuous supply of gaseous oxygen reference gas during the use of a probe for the direct determination of oxygen in molten steel involving the use of a solid electrolyte and a galvanic oxygen fuel cell principle, said method comprising: providing a preformed compressed mass of a Group II A metal peroxide, within a restricted zone including said solid electrolyte; decomposing said peroxide by the heat of the molten metal; and using the gaseous oxygen so-produced firstly to sweep stagnant gas from a zone at the base of the solid electrolyte, and secondly to bathe the solid electrolyte with said flowing, generated oxygen gas.

8. The method of claim **7** wherein the peroxide is barium peroxide.

9. A composition for forming the sub-assembly of claim **3** comprising: the intimate admixture of barium peroxide, aqueous sodium silicate and talc, in the form of screened, dried particles of 40 – 425 microns in size.

10. The composition of claim **9** in the form of a molded compressed hollow cylinder.

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