March 27, 1973 R. J. FRUEHAN ET AL 3,723,279

APPARATUS FOR OXYGEN DETERMINATION

Filed May 21, 1970 2 Sheets-Sheet 1

FIG. 1

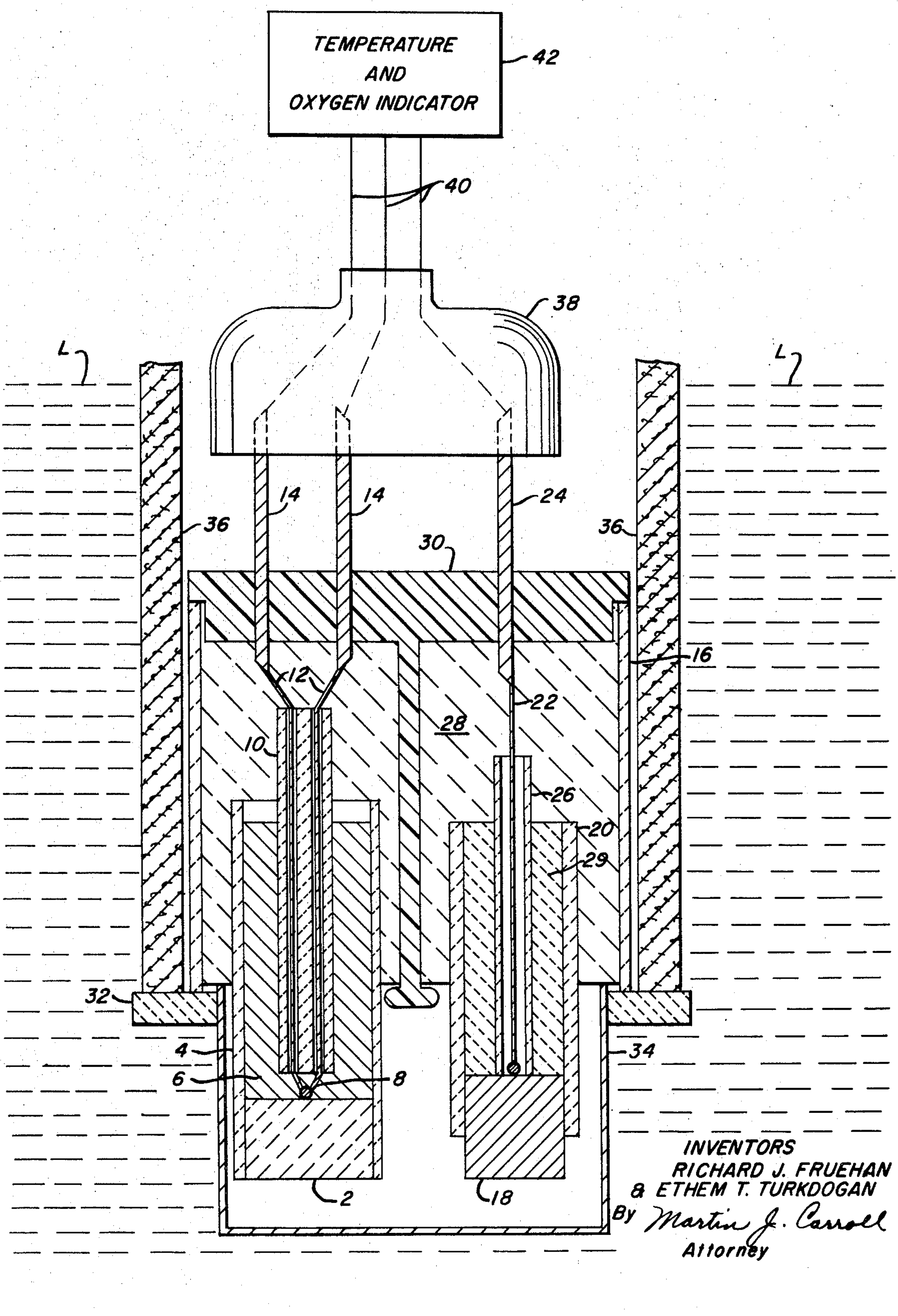

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FIG. 3

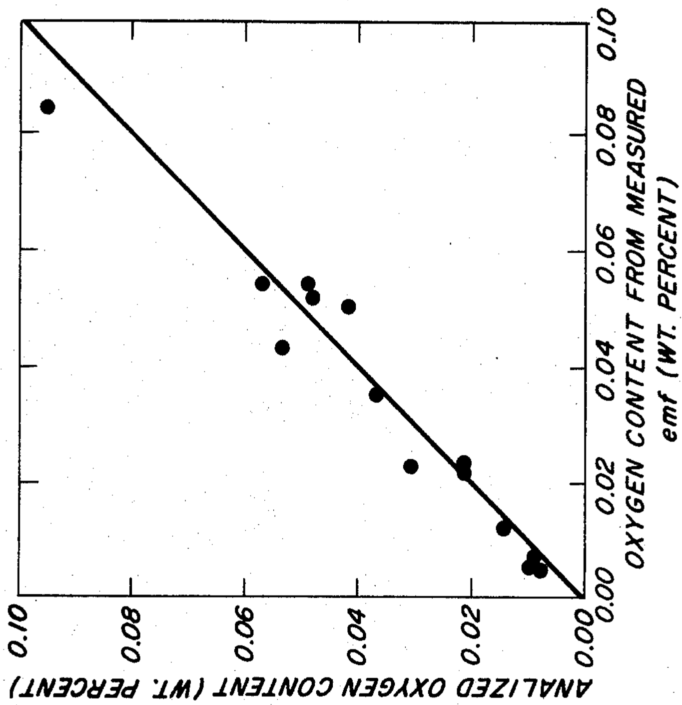
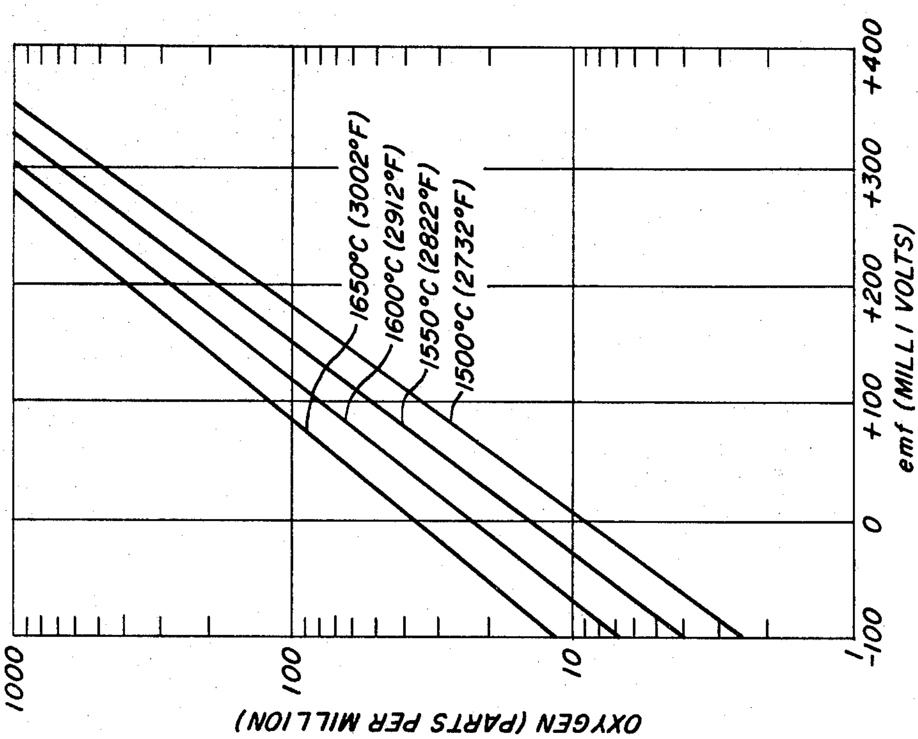


FIG. 2



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3,723,279

APPARATUS FOR OXYGEN DETERMINATION

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Continuation-in-part of application Ser. No. 727,314, May 7, 1968. This application May 21, 1970, Ser. No. 39,530
Int. Cl. G01n *27/46*
U.S. Cl. 204—195 S 10 Claims

ABSTRACT OF THE DISCLOSURE

A device for measuring oxygen content of fluids at elevated temperature comprises a galvanic cell with a solid oxide electrolyte and a reference electrode of a mixture of chromium or an alloy thereof and Cr_2O_3. When the fluid, acting as the other electrode, contacts the electrolyte, the resulting EMF indicates oxygen content. Provision is also made for simultaneous temperature determination and for electrical contact with fluids, such as liquid steel.

This application which is a continuation-in-part of our co-pending application, Ser. No. 727,314, filed May 7, 1968, now abandoned, 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 ladle or furnace without sampling. 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 liquid copper and hot furnace gases.

The steel-making process can be considerably advanced if the amount of oxygen dissolved in molten steel is continuously and immediately known during the various stages of the process. Such knowledge would permit previously impossible manipulations of a melt of steel by providing better control of the oxidation and deoxidation reactions.

The oxygen content of liquid steel has heretofore been determined by the analysis of samples of the liquid steel. The various analytical methods now used require elaborate equipment and do not provide results rapidly enough for best control of the steel-making process. A solid oxide electrolyte galvanic cell with a gaseous reference electrode has been used in laboratory experiments to provide a rapid determination of oxygen in liquid steels, but these cells are not practical for use in steel production for various reasons. They are relatively expensive, their accuracy is not satisfactory, and their quality is not uniform nor satisfactory.

According to our invention, we provide an oxygen cell having a solid oxide electrolyte fused in a refractory tube. A thermocouple is embedded into a condensed phase reference electrode which is placed inside the tube. The thermocouple, in addition to providing a temperature determination, serves as one connection to an oxygen indicating apparatus. A disc of molybdenum cermet which contacts the liquid steel is also connected to the oxygen indicating apparatus by a wire of the same material that connects the thermocouple to the oxygen indicating apparatus. A metallic cap, which dissolves in the liquid steel, protects the cell or probe from the slag when plunged into the melt. Within a few seconds after immersion in the liquid steel, a steady and reliable EMF is achieved which is measured by the oxygen indicating apparatus.

It is therefore an object of our invention to provide apparatus for rapid or continuous determination of the oxygen content in high temperature fluid over a wide range of temperatures.

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Another object is to provide a disposable probe for determining oxygen content in molten metal without sampling the melt.

A further object is to provide such a probe which is relatively inexpensive, reliable and accurate.

A still further object is to provide such a probe that requires no thermo-electromotive force corrections.

Still another object is to provide such a probe which also determines the temperature of the liquid metal.

These 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 the oxygen probe of our invention and includes its connections to be oxygen and temperature indicating apparatus;

FIG. 2 is a graph showing the relationship between the measured EMF and oxygen content in parts per million; and

FIG. 3 is a graph comparing the measured oxygen content of liquid steel with the oxygen content determined by the neutron activation method of analysis.

Referring more particularly to the drawings, reference numeral **2** indicates a calcia stabilized zirconia,

$$ZrO_2(CaO)$$

disc which is placed in one end of a refractory container **4**. Disc **2** may be fused to the bottom of a silica tube **4**, or inserted into the bottom of an alumina tube **4**. Disc **2** is preferably about 3 mm. in diameter and 3 mm. high. Contained in tube **4** above disc **2** is a mixture **6** of Cr and Cr_2O_3, about 90 to 98 weight percent Cr, the balance Cr_2O_3. Partially embedded in the mixture **6** is a conventional thermocouple **8** having a double bore silica tube **10** and a pair of wires **12**, preferably Pt-Pt/10% Rh in contact with the mixture **6**. The upper ends of wires **12** are each connected to contact prongs **14**. Tube **4**, thermocouple **8** and part of prongs **14** are enclosed in an alumina container tube **16**. A disc **18** of molybdenum cermet, approximately 75 to 85 weight percent Mo and the balance Al_2O_3, is fitted tightly into the bottom of a silica tube **20** to prevent the penetration of liquid metal into the inside of tube **20**. A Pt wire **22** is attached to disc **18** and to a contact prong **24** through a silica protective tube **26**. Tube **16** is filled with a refractory cement **28**, such as Alundum, which is an electrical and thermal insulator. Tube **20** is filled with alumina powder **29**. The top of tube **16** is covered with a cap **30** made of a plastic, such as Teflon. Prongs **14** and **24** project through cap **30** to form an electrical plug. An alumina support ring **32** is attached to the bottom of tube **16**. The bottom of tube **16** is sealed by a metal cap **34**. A long protective cardboard tube **36**, only a portion of which is shown, rests on support rings **32**. A receptacle **38** fits over prongs **14** and **24** with lead wires **40** connecting prongs **14** and **24** to a temperature and oxygen indicator **42**. Prongs **14** and their respective lead wires **40** are compensating alloys conventional for a Pt-Pt/10% Rh thermocouple. Prong **24** and its lead wire **40** is the same compensating alloy as that connected to the Pt thermocouple wire. Indicator **42** is preferably a potentiometric recorder or similar device with two indicating arms. One indicating arm, for indicating temperature, is connected to wires **12**. A second indicating arm, indicating in the range of minus 0.2 volt to plus 0.5 volt, is for oxygen content, and is connected to wire **22** and Pt wire **12**.

In operation, the probe is plugged into a permanent receptacle provided at the furnace or ladle above the liquid metal L and then plunged into the melt to a suitable depth. The cardboard tube **36**, which extends above the top of the melt, protects the wires and upper elements of the probe from damage by the metal. If the protective cardboard tube causes significant local carbon deoxidation, this may be overcome by replacing the last few inches of the cardboard tube with a refractory tube, such as silica. Cap **34** protects the probe from chemical attack by the slag as the probe is lowered through the slag into the molten metal. The cap **34** is made of material, such as copper or brass, which will not affect the oxygen content of the steel and which readily dissolves in the steel so as to expose the electrolyte and the molybdenum cermet disc to the molten steel. The cap **34** may also be made of steel. When the stabilized zirconium oxide electrolyte contacts the electrode of liquid steel, a galvanic cell results which may be represented as follows:

$$Pt(s),\ Cr(s)+Cr_2O_3(s)|ZrO\ (CaO)\ (s)|Fe\text{-}O\ (1),\ (Mo\ cermet),\ Pt(s)$$

The voltage across the electrolyte is given by the free energy equation as follows:

$$E=2.303\,\frac{RT}{nF}\log\frac{[\text{percent O}]}{K_{p_{O_2}}{}^{1/2}} \quad (1)$$

where:

E=The voltage across the electrolyte in volts
R=1.987 cal./g.-atom deg., the gas constant
T=Temperature in degrees Kelvin
n=2, the number of equivalents per gram-atom for oxygen
F=23,061 cal./equivalent-volt, the Faraday constant
p_{O_2}=The dissociation pressure of Cr_2O_3 in equilibrium with chromium
K=The equilibrium constant for reaction of oxygen with liquid iron

$$\tfrac{1}{2}\ O_2\ (\text{g. 1 atm.})=O\ (\text{1 wt. percent in Fe}) \quad (2)$$

The temperature dependence of the equilibrium constant K and $p_{O_2}{}^{1/2}$ for Cr-Cr_2O_3 equilibrium from known thermodynamic data is

$$\log K=\frac{6120}{T}+0.15 \quad (3)$$

$$\log p_{O_2}{}^{1/2}\ (\text{atm.}^{1/2})=-\frac{19,700}{T}+4.47 \quad (4)$$

By combining these equations and substituting values of the constants, the following equation is obtained for weight percent oxygen in liquid steel in terms of EMF, (E) in milivolts and T in degrees Kelvin for the Cr-Cr_2O_3 reference electrode

$$\log\ (\text{percent})\ O=4.62-\frac{13,580-10.08\ E}{T} \quad (5)$$

It should be noted that E is actually a measure of the oxygen activity in liquid steel. The relationship of the activity of the oxygen in the liquid steel to the oxygen content of the liquid steel is well known and is shown in FIG. 2 where the EMF indicates the oxygen activity.

By using lead wires to the oxygen indicator of the same material, preferably platinum, no thermo-electromotive force corrections are required since all connections are at the liquid metal temperature and the lead wires will be at the same temperature. Fusing a small disc of electrolyte into the silica tube greatly increases its resistance to thermal shock.

While the EMF of Equation 5 neglects the effect of alloying elements in steel, the equation is essentially correct for low alloy steels. An approximate correction for alloying elements can be made by the following expression:

$$\text{Actual log (wt. percent O)}=\text{Apparent log (percent O)}-(e_i\ \text{percent}\ i+e_j\ \text{percent}\ j+e_k\ \text{percent}\ k+\ldots) \quad (6)$$

where:

apparent log percent O=the value from Equation 5 using measured E

percent i, percent j, percent k, etc.=concentrations of various alloying elements in liquid steel, such as Mn, Si, C, etc.
e_i, e_j, e_k, etc.=interaction coefficients for various alloying elements.

For large tonnage, low carbon steel-making the concentrations of Mn, Si, C . . . are smal lenough that the above correction becomes insignificant for all practical purposes.

A steady EMF is achieved in a few seconds after plunging the probe into the melt and provides continuous oxygen content readings up to 40 minutes. The cell has sufficient reliability and accuracy for use in the steelmaking process as shown in FIG. 3 where the oxygen content of samples determined by the neutron activation method is compared with the oxygen content as measured by the EMF of the cell.

While the specific components set forth above are preferred since they have proven very successful in use in determining the oxygen content of liquid steel, they may be varied as long as they meet the following requirements. The electrolyte **2** must be a solid oxide and an oxygen ion conductor with insignificant electronic conductivity under the conditions of its use, particularly at the temperature and oxygen partial pressure to which it is subjected. It must not react with the materials it contacts. ZrO_2 with 3 to 10% by weight of CaO and ThO_2 with 3 to 20% by weight of Y_2O_3 are preferred for use with steel. MgO, Al_2O_3, and ZrO_2 with 3 to 10% by weight of MgO or Y_2O_3 and ThO_2 with La_2O_3 may also be used, but electrolytes are not all suitable for use with all types of fluids.

The reference electrode **6** must be a condensed phase mixture of chromium and its oxide which does not readily melt at the temperature to which it is subjected nor react significantly with the materials it contacts. It is preferred to use a mixture of between about 90% to 98% by weight of pure chromium and the remainder Cr_2O_3. However, a chrome alloy may be substituted for the chromium. The alloying metal must be one having an oxide less stable than Cr_2O_3 so that Cr_2O_3 will be the equilibrium oxide phase. The melting point of the alloy must be high enough so that the alloy is solid at temperature of use. The dissociation pressure in Equation 1 would be corrected accordingly. Suitable alloys include up to 10% by weight of manganese or iron, or up to 5% nickel.

While it is preferred to use a Mo cermet (80% Mo, 20% Al_2O_3) for member **18**, it is only necessary that the material be an electronic conductor, will not melt at its temperature of use, will not readily dissolve in the fluid so that a steady and reliable voltage reading can be taken, and when dissolved in the liquid will not affect the voltage reading. Such materials are Cr cermet (80% Cr, 20% Al_2O_3), Cr_2O_3, Mo wire or rod, Fe wire or rod and graphite rod. Not all materials can be used for all types of liquids.

A probe suitable for determining the oxygen content of liquid copper may have a reference electrode of Cr-Cr_2O_3, and a liquid metal contact of Cr cermet or Cr_2O_3.

When used for determining the oxygen contents of the gases in soaking pits, heat treatment furnaces, hot exhaust gases or the like, the probe is altered slightly. Wire **22** must contact the electrolyte **2** where it is in contact with the gas and the cermet contact may be omitted. The balance of the probe is, of course, not in contact with the gas.

The specific probe described has been used in the oxygen content range from about 10 p.p.m. to about 1000 p.p.m. Below that concentration it is preferred to use $ThO_2(Y_2O_3)$, which will provide predominantly ionic conduction at oxygen contents down to 1 p.p.m.

While silica has been used extensively in the probe, other refractories, such as alumina, may be used which would better resist the effects of liquid steel. The refractory must, of course, not react with other components of the probe.

Since the probe is made of inexpensive materials and is relatively easy to manufacture, the probe can be used once and thrown away in the same manner that immersion thermocouples are used. Because a conventional thermocouple is incorporated into the probe, temperatures may be determined at the same time as oxygen content, and auxiliary equipment requirements are minimal.

While the preferred embodiment of our invention is described as an instrument to use in a vessel, ladle or furnace as a conventional immersion thermocouple is used, other adaptations are possible. As an example, a zirconia thimble, small enough to avoid thermal shock, could be located in the lining of a tundish to contact the liquid steel with the other essential parts of the probe arranged in a manner already described.

While several 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 determining the oxygen content of a fluid at a temperature of at least 700° C. which comprises a galvanic cell including a refractory container closed at one end thereof by a solid oxide electrolyte adapted to contact said fluid, and a reference electrode inside said refractory containers and in electrical contact with said electrolyte, said electrolyte being an oxygen ion conductor having insignificant electronic conductivity under conditions of use, said reference electrode being a mixture of Cr_2O_3 and a material of the class consisting of chromium and an alloy of chromium with a metal having an oxide less stable than Cr_2O_3, said material having a melting point such that it will be solid at the temperature of said fluid, and means for measuring the EMF of the cell when the electrolyte contacts the fluid.

2. Apparatus according to claim **1** in which said electrolyte is of the group consisting of MgO, Al_2O_3, ZrO_2 with 3 to 10% by weight of CaO, ThO_2 with 3 to 20% by weight of Y_2O_3, ZrO_2 with 3 to 10% by weight of MgO, ZrO_2 with 3 to 10% by weight of Y_2O_3, and ThO_2 with La_2O_3.

3. Apparatus according to claim **1** which includes a refractory electronic conductor adapted for electrical contact with said electrolyte, said conductor being made of material which is relatively insoluble in said fluid, and means connecting said conductor and said reference electrode to said EMF measuring means.

4. Apparatus according to claim **3** in which said conductor is of the group consisting of a molybdenum cermet composed of about 80% by weight of Mo and about 20% by weight of Al_2O_3, a chromium cermet composed of about 80% by weight Cr and about 20% by weight of Al_2O_3, molybdenum, graphite and Cr_2O_3.

5. Apparatus according to claim **4** in which said EMF measuring means is a two position potentiometric recorder; and which apparatus includes a thermocouple, said thermocouple having a junction embedded in said reference electrode, a first thermocouple wire connected to both potentiometric positions, and a second thermocouple wire connected to one potentiometric position to indicate temperature; and in which said means connecting said conductor to said EMF measuring means includes a junction of said conductor and a wire of the same material as said first thermocouple wire, said last named wire being connected to the other potentiometric position to indicate oxygen content, and said junctions being located to operate at the same temperatures under conditions of use.

6. Apparatus according to claim **1** in which said electrode is a mixture of between about 90% to 98% by weight of chromium and the remainder Cr_2O_3.

7. Apparatus according to claim **6** for use in a melt of steel having a layer of slag thereon, which apparatus includes a steel-soluble cap shielding said apparatus from slag upon immersion with said melt, said cap being of the group consisting of copper, brass, and steel.

8. Apparatus according to claim **7** which includes a refractory electronic conductor adapted to contact said melt, said conductor being made of material which is relatively insoluble in said melt, and means connecting said conductor and said reference electrode to said EMF measuring means.

9. Apparatus according to claim **1** in which said material of said reference electrode is an alloy of chromium with another metal.

10. Apparatus according to claim **9** in which said alloying metal is of the group consisting of up to 10% by weight manganese, up to 10% by weight iron and up to 5% by weight nickel.

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TA-HSUNG TUNG, Primary Examiner

U.S. Cl. X.R.

204—1 T

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,723,279 Dated March 27, 1973

Inventor(s) RICHARD J. FRUEHAN, ET. AL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 14, "be" should read -- the -- . Column 3, line 47, "milivolts" should read -- millivolts -- ; line 50, "(percent) 0" should read -- (percent 0) -- . Column 4, line 7, "smal lenough" should read -- small enough -- . Column 5, line 28, "containers" should read -- container -- .

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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