United States Patent

Franz

[15] **3,642,599**

[45] **Feb. 15, 1972**

[54] SOLID ELECTROLYTE PROBE FOR DETERMINING THE OXYGEN CONTENT OF MOLTEN MATERIALS

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[22] Filed: **May 12, 1969**

[21] Appl. No.: **823,701**

[52] **U.S. Cl.** **204/195**

[51] **Int. Cl.** **G01n 27/30**

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

[56] **References Cited**

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[57] **ABSTRACT**

A solid electrolyte probe for direct immersion into a molten material, such as molten copper, to determine the oxygen content thereof. A tubular receptacle fabricated from a solid electrolyte, such as stabilized zirconia, and adapted to hold an oxygen-containing material, has its open upper end protectively closed by a vertically elongate, relatively massive, refractory cap which has a longitudinal passage therethrough to accommodate the electrical lead for the probe electrode and is long enough to protect the tubular receptacle against both unrepresentative, high-oxygen molten material and the molten material-air interface, and to protect both the tubular receptacle and the electrical conductor against splash of the molten material that could otherwise lead to short circuiting of the electrical signals.

7 Claims, 3 Drawing Figures

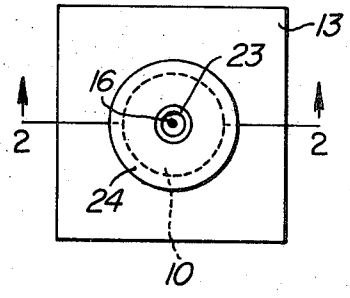
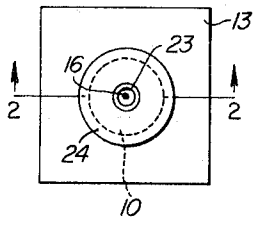


FIG. 1.



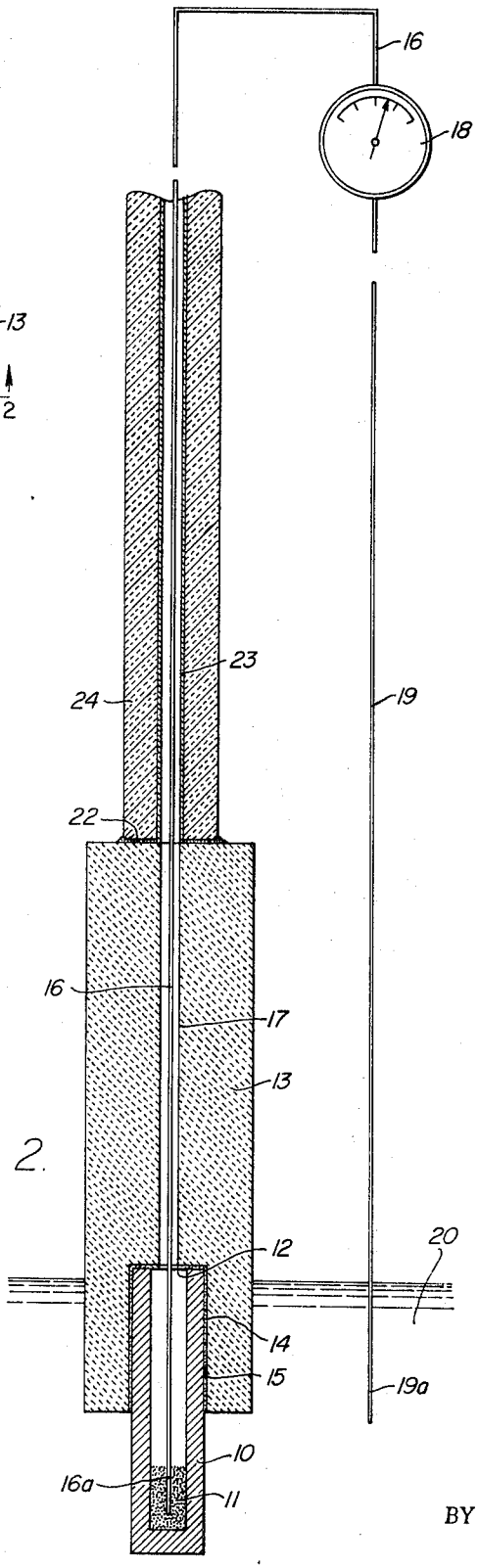


FIG. 2.

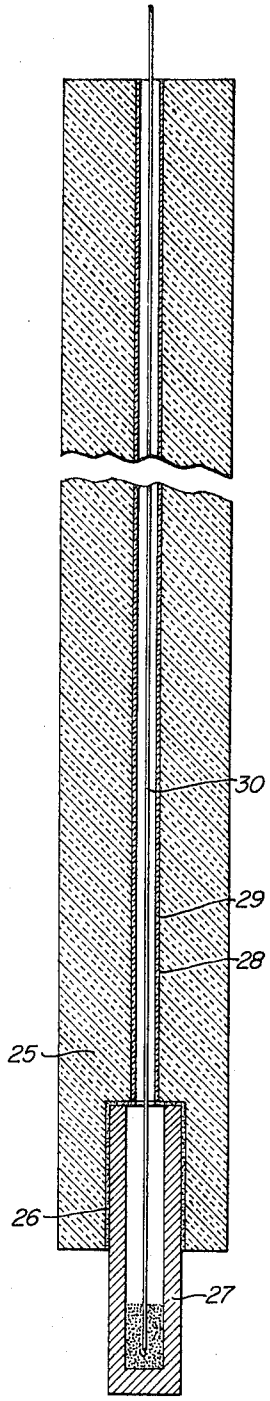


FIG. 3.

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SOLID ELECTROLYTE PROBE FOR DETERMINING THE OXYGEN CONTENT OF MOLTEN MATERIALS

BACKGROUND OF THE INVENTION

Field

The invention has to do with determination of the oxygen content of molten materials, especially molten metals such as copper, and is particularly concerned with the construction of probes for direct immersion into the molten material. Considerable experimental work has been done in the past to adapt, to the quantitative determination of oxygen in molten materials, the known capability of certain refractory oxides, such as lime-stabilized zirconia, to act as a solid electrolyte for the transport of oxygen ions. Tubular receptacles made wholly or partially of stabilized zirconia and containing an oxygen source material and an electrode have been used in this work.

Objective

Although all molten materials present problems of thermal shock and shielding with respect to oxygen-determination probes of the general type concerned, I have found that molten copper presents special problems that may or may not be shared by other molten materials, depending upon their characteristics. Thus, I have found that molten copper, having relatively low oxygen content, as does commercial wire bar copper, presents a zone rising about 6 inches above the surface thereof wherein there is a "rain" of small, gas-borne droplets of copper that tend to collect and coalesce on the upper, exposed surface of commonly available, relatively short probe tubes made of the solid electrolyte, and bridge over the probe tube opening, causing short circuiting of the probe and yielding unrepresentative results because of the higher oxygen content of copper at and near the copper-air interface. Closing of the probe tube opening and protecting of the upper portions of the tube against contact by unrepresentative portions of the molten copper present problems from both functional and economic standpoints. Providing a practical solution to these problems was the objective in the making of the present invention.

State of the Art

Solid electrolyte probes of the type concerned have heretofore utilized tubes of the solid electrolyte material, with or without structural integration with a special electro-chemical cell, as in the McPheeter et al. U.S. Pat. No. 3,309,233. Thermal shock has been a cause of tube failure, especially when the molten material being tested is a molten metal. For this reason tubes of fused quartz, with bottom-forming inserts of the solid electrolyte, have been developed and successfully used in determining the oxygen content of molten steels, see the technical article by G. R. Fitterer entitled "Further Development of the Electrolytic Method for the Rapid Determination of Oxygen in Liquid Steels," Journal of Metals, Sept. 1967, pp. 92–96.

SUMMARY OF THE INVENTION

In accordance with the invention, problems encountered in the attempted use of the commonly available, relatively short tubes of solid electrolyte have been solved in a very effective manner by utilizing an elongate, massive cap of an electrically nonconductive, common refractory material. Thus, a longitudinal section of an ordinary refractory brick, drilled at one end to receive an upper portion of the probe tube and drilled through the remainder of its length to accommodate the electrical lead for the electrode positioned within the probe tube, may be advantageously employed. Although use of a refractory brick is a very economical way of accomplishing the purposes of the invention, the cap may also be made by suitably drilling or boring a length of silicon carbide rod and inserting a tube of electrical insulating material such as glass within the lead-wire-receiving passage, or by molding a conventional, refractory, "ramming" mix about a relatively thin-walled form tube of electrical insulating material. However fabricated, the protective cap is massive relative to the probe tube and of a considerably greater length.

By the term "massive" is meant an elongate block of the refractory material, substantially uniform in cross section and solid except for the tube-insert recess at one end and the relatively attenuate passage therethrough for accommodating the electrode lead. The thickness of the walls defining the tube-insert recess are at least twice that of the walls of a probe tube capable of resisting the thermal shock encountered during immersion in the molten material, and the overall length of the cap is several (at least three) times the length of the probe tube.

THE DRAWING

In the accompanying drawing, which illustrates a form of the invention presently contemplated as the best mode of carrying it out in actual practice;

FIG. **1** represents a top plan view of the probe as covered with a massive cap in accordance with the invention;

FIG. **2**, a view in vertical section taken on the line **2**—**2** of FIG. **1** and showing the probe in operative position in a bath of a molten material, the electrical circuit being indicated schematically; and an protective tube added for the lead wire above the cap;

FIG. **3**, a similar view showing a somewhat different embodiment of the invention.

DETAILED DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

In the illustrated form of FIGS. **1** and **2**, the probe of the invention comprises a tubular receptable **10** fabricated from a solid electrolyte, such as stabilized zirconia, and adapted to receive and hold an oxygen-containing material **11**, such as a nickel, nickel oxide mixture, as an oxygen ion reference source. The probe tube **10** has its upper end open as at **12**.

A relatively elongate and massive cap **13** for the open upper end of the probe tube **10** is provided by a longitudinal half-section of an insulating fire brick that has been cut lengthwise midway of its breadth, i.e., that has been cut in two lengthwise midway of and along its opposite broad faces. Such longitudinal half-section constitutes a relatively elongate and massive block, and has a hole bored into the center of one of its ends to provide a receiving recess **14** for the open upper end of probe tube **10**. The depth of the hole is not critical, so long as there is enough overlap of the probe tube by the cap to provide stable securement between the two when cemented together. The fit is not so tight as to preclude cementing by a refractory cement **15**.

To provide for entry into the probe tube **10** of an electrical lead **16**, whose end constitutes an electrode **16***a*, a relatively attenuate hole or passage **17** is drilled longitudinally through cap **13** from end to end thereof and communicating with recess **14**. Lead **16** and electrode **16***a* are preferably provided by a length of high-temperature-resistant alloy wire, such as the commercial product "Kanthal," passed through such passage **17** and dipping into the material **11** internally of the probe. It is connected in circuit, externally of the probe, with a high impedance meter **18** that will measure voltage with very little if any current flow, and with a second electrical lead **19** providing a second electrode **19***a* immersed in a bath of molten material **20**, such as wire bar copper. The second lead **19** and electrode **19***a* are preferably of the same alloy wire as the first.

The cap **13** should be at least 6 inches long. When made as indicated above from a standard insulating fire brick, it will usually be 8 or 12 inches long, depending upon the length of the brick. This is in contrast to the probe tube, which is about 2 inches long. The wall thickness of the probe tube is normally ⅛ of an inch, while that of the cap at the narrowest is normally ¾ of an inch.

It may be desirable, depending upon the type of furnace involved, to provide protection for the electrical lead wire **16** in the furnace atmosphere above the melt. For this purpose there extends upwardly from securement to the top of cap **13**, as by

refractory cement **22**, an elongate tube **23** of glass, fused silica, or other heat-resistant and electrical insulating material surrounded by a refractory material, such as silicon carbide **24**, or, if there is a reducing atmosphere in the furnace, graphite. The lead wire passes through the interior of tube **23**.

The probe tube as so constructed is suspended over and partially in the bath of material to be tested for oxygen content by means of a suitable harness, which forms no part of the invention and is not illustrated.

In the embodiment of FIG. **3**, the cap **25** is conveniently made by counterdrilling or boring a silicon carbide tube of appropriate length and diameter or thickness to provide a receiving recess **26** for the probe tube **27** that opens into the bore **28** of the tube into which is inserted a tube **29** of electrical insulating material for the lead wire **30**.

Other suitable high-temperature refractory material can be substituted for the silicon carbide. Moreover, the entire cap can be molded to shape from a refractory ramming mix cast around a tube of electrical insulating material and the upper part of a probe tube or suitable form.

Whereas this invention is here illustrated and described with respect to preferred forms thereof, it should be realized that various changes can be made.

I claim:

1. A solid electrolyte probe for determining the oxygen content of molten materials, comprising

a tubular receptacle fabricated from a solid electrolyte to provide walls of thermal-shock-resistant thickness, said receptacle having an open upper end and being adapted to receive and hold an oxygen-containing material as an oxygen ion reference source;

a protective cap for said receptacle in the form of an elongate and relatively massive block of refractory material having substantially uniform cross section throughout its length and recessed at one end to closely receive the open upper end of said receptacle and to surround it with a refractory shield, said cap being solid except for said recessed end and for a relatively attenuate passage extending longitudinally therethrough to accommodate an electrode lead wire, and the said open upper end of the receptacle being engaged by and occupying substantially the entire recess of said recessed end of the cap, the walls of said cap that define the receptacle-receiving recess being at least twice as thick as the walls of the receptacle, and the length of the cap being at least three times the length of the receptacle.

2. A probe according to claim **1**, wherein the refractory cap is a section of an insulating firebrick that has been cut into longitudinal half-sections midway of its breadth and that is substantially square in cross section.

3. A probe according to claim **2**, including oxygen-containing material within the receptacle, and an electrode in said material, said receptacle being cemented into the refractory body.

4. A probe according to claim **2**, wherein there is additionally provided an upward extension of the protective cap for protecting the electrode lead wire from the furnace atmosphere.

5. A probe according to claim **4**, wherein the attenuate passage through the upward extension of the cap is lined with a high-temperature-resistant and electrically nonconductive material.

6. A probe according to claim **1**, including oxygen-containing material within the receptacle, and an electrode in said material, said receptacle being cemented into the refractory body.

7. A probe according to claim **1**, wherein the attenuate passage through the cap is lined with a high-temperature-resistant and electrically nonconductive material.

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