Feb. 12, 1974 MAKOTO NODA ET AL 3,791,954

DEVICE FOR MEASURING OXYGEN CONCENTRATION OF MOLTEN METAL

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FIG. 1

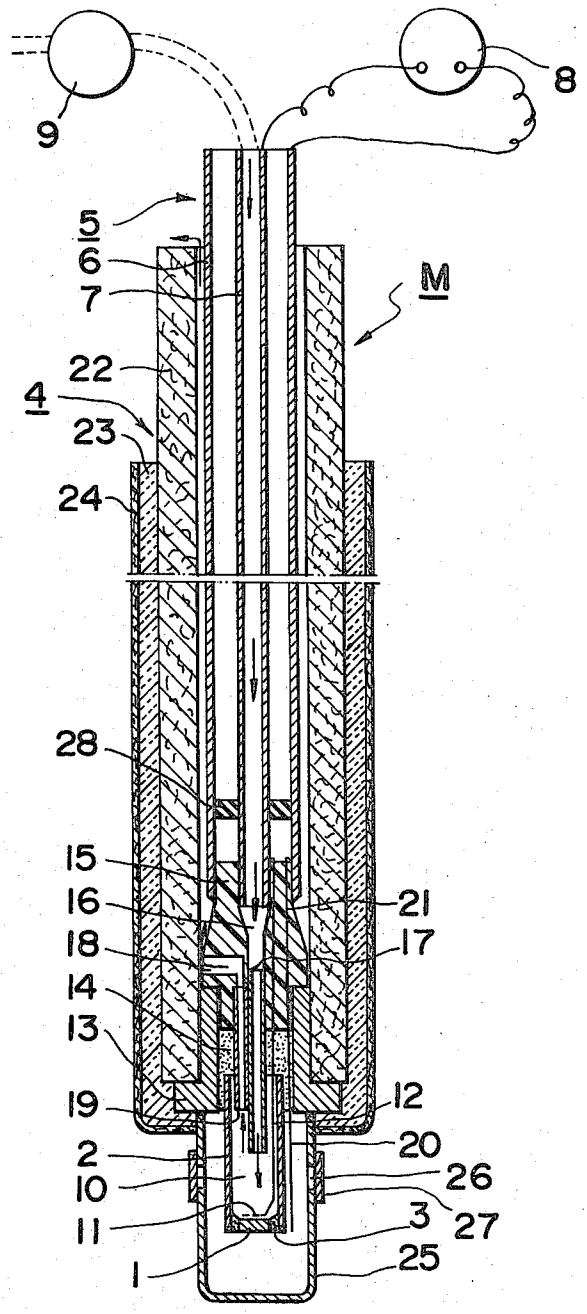


FIG.2

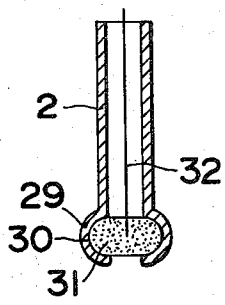


FIG.3

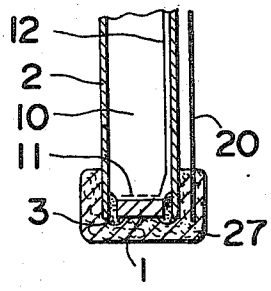


FIG.4

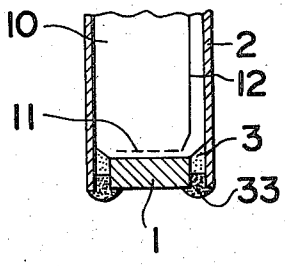


FIG.5

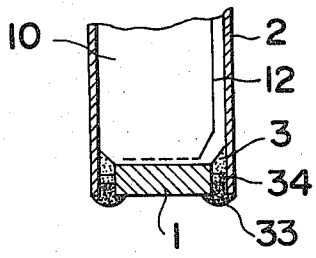


FIG.6

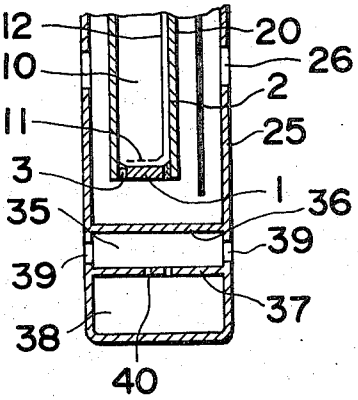
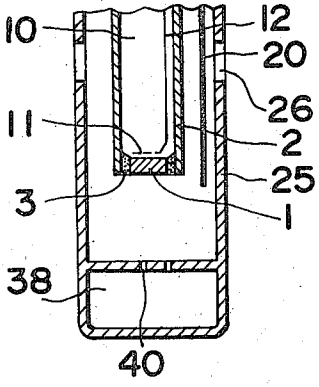


FIG. 7



DEVICE FOR MEASURING OXYGEN CONCENTRATION OF MOLTEN METAL

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FIG.8

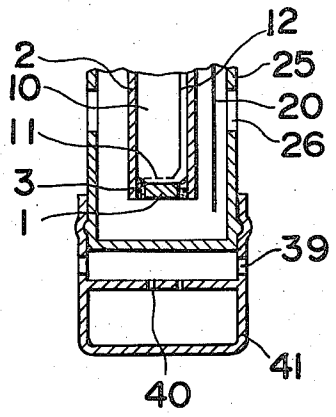
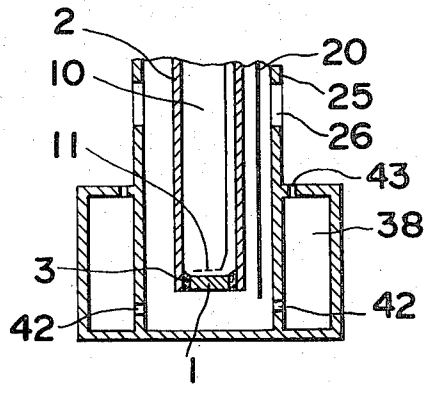


FIG.9



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3,791,954

DEVICE FOR MEASURING OXYGEN CONCENTRATION OF MOLTEN METAL

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Int. Cl. G01n 27/46
U.S. Cl. 204—195 S 7 Claims

ABSTRACT OF THE DISCLOSURE

A device for measuring oxygen concentration of molten metal by using an oxygen concentration cell, wherein a solid electrolyte is directly or indirectly covered with a material to be carbonized in the molten metal, so that the element may be gradually heated before coming in contact with the molten metal. The electric connection of the solid electrolyte to an indicator may simultaneously be accomplished with its mechanical connection to a standard gas source. A specimen of the clean molten metal can be collected from substantially the same spot where the oxygen concentration is measured.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a device for measuring oxygen concentration of molten metal, and more particularly to a device for measuring oxygen concentration of molten metal by using an oxygen concentration cell with a solid electrolyte.

It is well known to make an oxygen concentration cell by a solid electrolyte consisting essentially of a solid solution of at least one oxide selected from the group consisting of zirconium oxide (ZrO_2), hafnium oxide (HfO_2), cerium oxide (CeO_2), and thorium oxide (ThO_2), and at least one oxide selected from the group consisting of magnesium oxide (MgO), calcium oxide (CaO), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), neodymium oxide (Nd_2O_3), barium oxide (BaO), strontium oxide (SrO), selenium oxide (Se_2O_3), ytterbium oxide (Yb_2O_3), and samarium oxide (Sm_2O_3). Theoretically, the EMF of such solid electrolyte at a temperature T(° K.) for an oxygen partial pressure ratio P_2/P_1 across its opposite surfaces is given as follows:

$$EMF=\frac{RT}{4F}\ln\frac{P_2}{P_1}$$

Here, R is the gas constant, and F is the Faraday constant.

Based on the above equation, it is possible to determine an unknown oxygen partial pressure P_2 by measuring the EMF and the temperature while exposing the solid electrolyte to a known oxygen partial pressure P_1 at its one surface and to the unknown oxygen partial pressure P_2 at its opposite surface. Therefore, it is possible to determine an unknown oxygen concentration, based on the partial pressure thus determined.

The concentration of free oxygen (namely, oxygen concentration) in a molten metal can be determined by using such a solid electrolyte, based on the aforesaid principles; for instance, voltage-oxygen concentration curves may be predetermined for a given solid electrolyte so that an unknown oxygen concentration may be determined by measuring the EMF of the electrolyte while exposing it to the unknown oxygen concentration and entering the EMF to the predetermined curves.

Actually, measurement of the oxygen concentration in molten metal is carried out by dipping a solid electrolyte therein, which electrolyte is secured to the tip of a tubular holder made of refractory material, such as alumina porcelain or quartz glass.

Description of the prior art

Conventional devices for measuring the oxygen concentration of molten metal by using a solid electrolyte have a shortcoming in that the solid electrolyte is highly susceptible to cracks due to the thermal shock when it is dipped into the molten metal. In order to avoid such cracks, it has been practiced to preheat the solid electrolyte secured to the tip of its holder before dipping it into a molten metal. Such preheating, however, is not only time-consuming but also unreliable, because its success depends on the operator's skill and experience.

The conventional devices are also susceptible to measuring errors due to the presence of slag on the top surface of molten metal being measured. More particularly, when the solid electrolyte carried by a tubular holder is dipped into the molten metal, it passes through a layer of slag floating on the surface of the molten metal, and such slag sticks to the surface of the solid electrolyte so as to prevent the molten metal from coming in direct contact with the solid electrolyte. The presence of slag between the molten metal and the solid electrolyte tends to cause an error in the measurement.

With the conventional devices for measuring oxygen concentration of molten metal by using solid electrolyte, it has been noticed that the gastight joint between the solid electrolyte and the tip of its holder is rather quickly deteriorated due to the difference of the thermal expansion therebetween when the device is dipped into the molten metal. Therefore, the oxygen gas partial pressure ratio across the solid electrolyte is affected and an error is caused in the measurement of the oxygen gas concentration.

Various approaches have been tried for improving the bondage, gastightness, and refractory adhesive of the joint between the solid electrolyte and its holder. For instance, the oxides constituting the solid electrolyte is granulated, so as to have a certain grain size distribution, and the oxide thus granulated is made into a paste by kneading it while adding a solution of a phosphate or acetate of that metal whose oxide constitutes the solid electrolyte, which paste is stuffed in the gap between the solid electrolyte and its holder. The salts in the paste are decomposed by a high temperature to obtain desired improvement of the bondage, gastightness, and the refractory adhesive of the aforesaid joint. Furthermore, it has also been tried to further improve the bondage and gastightness of the aforesaid joint by causing heat-shrinkage at the tip of the tubular holder of the solid electrolyte by using high-temperature flame of oxygen and hydrogen. Despite such efforts, it is impossible to establish accurate coincidence of the thermal expansion between the solid electrolyte and its tubular holder. Accordingly, it is still very difficult to ensure high gastightness between the electrolyte and its tubular holder by completely eliminating the risk of generating minute gaps therebetween due to the difference of thermal expansion therebetween.

In conventional oxygen concentration measuring devices, an elongated hollow protective tube made of steel or bias-wound paper is used for facilitating the immersion the solid electrolyte secured to the tip of the tubular holder into molten metal. (Such steel and paper tubes are also used for carrying and protecting samplers for taking specimens to be used in chemical analysis.) Since the steel is heavy and difficult to handle, paper is widely used. Such paper tubes, however, have a shortcoming in that when they are dipped in the molten metal, the paper form-

ing the tube is carbonized starting from the outer surface thereof, and the molten metal flows into the paper tube in 15 to 20 seconds after dipping into the molten metal. Accordingly, if any measuring means protected by such a paper tube is kept in the molten metal more than 15 to 20 seconds, the measuring means is likely to be damaged by the molten metal rushing into the protective tube.

It is preferable to correct the value determined by the solid electrolyte for the effect caused by co-existing elements.

Other elements co-existing in the molten metal may affect the measurement of free oxygen therein, so that the value of the oxygen concentration determined by the solid electrolyte should preferably be corrected for such effect of other elements. To this end, a specimen for chemical analysis is taken from the molten metal by using a dipper, so as to determine the contents of other elements co-existing in the molten metal at the time of the measurement. The conventional dipper for taking such specimens, however, has a shortcoming in that they take slag together with the molten metal, so that the chemical analysis of the specimen taken by such dipper does not provide the true contents of various elements of the molten metal, but the result of the chemical analysis is likely to be affected by the slag. Accordingly, the accuracy of the correction by using such a conventional dipper is rather low.

The amount of total oxygen in the form of free oxygen and oxides, such as ferric oxide (Fe_2O_3), aluminum oxide (Al_2O_3) and so on, in the molten metal is also determined by means of chemical analysis or radio-activation analysis for comparison with the free oxygen concentration determined by the solid electrolyte. The specimen, however, is likely to contain slag, because when the dipper is removed from the molten metal the dipper scoops slag floating on the surface of the molten metal. Thus, the sample does not represent the true composition of the molten metal, and the accuracy or significance of the amount of total oxygen as determined by using such sample is fairly low. A special dipper may be used for taking pure specimen without any slag, for improving the accuracy of the amount of the total oxygen, but if such dipper takes specimen at a position distant from the position of the oxygen concentration cell, the merit of adding the two measured values taken substantially at the same position is almost lost. Besides, separate sampling before or after the measurement by using the oxygen concentration cell is a time-consuming and troublesome operation.

In an oxygen concentration measuring device using a solid electrolyte, it is necessary to provide two kinds of connections; namely, an electric connection between the solid electrolyte, and a mechanical connection for providing a standard gas to one side of the solid electrolyte. There has been a need for a simple mechanism capable of simultaneously accomplishing the aforesaid two connections, but no one has succeeded yet in providing such a mechanism.

SUMMARY OF THE INVENTION

Therefore, the principal object of the present invention is to provide a device for acurately measuring the oxygen concentration of molten metal, which device is free from any of the aforesaid difficulties experienced in conventional devices for measuring oxygen concentration.

An object of the present invention is to provide a device for measuring oxygen concentration of molten metal by using a solid electrolyte, which device eliminates the risk of generating cracks in the solid electrolyte, so as to allow its dipping into a molten metal to be measured without preheating the solid electrolyte together with its tubular holder.

Another object of the present invention is to provide a device for measuring oxygen concentration of molten metal by using a solid electrolyte, which device can prevent slag of the molten metal from entering between the surface of the solid electrolyte and the molten metal when the device is dipped in the molten metal, so that solid electrolyte comes in contact with clean molten metal free from slag.

Another object of the present invention is to provide a device for measuring the oxygen concentration of molten metal of the aforesaid type, which ensures gastight bondage of the solid electrolyte to its holder even if it is dipped in the molten metal.

It is an object of the present invention to provide a simple device for measuring oxygen concentration of molten metal, which can be kept in the molten metal for a time period long enough for ensuring stable measurement. The measuring device may be equipped with a means for taking specimen of the molten metal for laboratory analysis.

Another object of the present invention is to provide a device for measuring oxygen concentration of molten metal, which simultaneously measures the oxygen concentration and collect a clean specimen of the molten metal for laboratory analysis, the composition of the specimen thus collected being substantially identical wiht that of the molten metal whose oxygen concentration is measured by the device at the time of the collection.

Another object of the present invention is to provide a device for measuring oxygen concentration of molten metal by using a solid electrolyte, in which electric connection from the solid electrolyte to an outside circuit is accomplished simultaneously with mechanical connection of the solid electrolyte to a standard gas supply passage.

BRIEF DESCRIPTION OF THE DRAWING

The foregoing objects and other objects as well as the characteristic features of the invention will become more apparent and more readily understandable by the following description and the appended claims when read in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic vertical sectional view of preferred embodiment of a device for measuring oxygen concentration of molten metal, according to the present invention; and

FIGS. 2 to 9 are setional views of different embodiments of the essential portion of the device of FIG. 1.

Like parts are designated by like numerals throughout the drawings.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1, a device for measuring oxygen concentration of molten metal comprises a solid electrolyte or a ceramic disk **1** gastightly secured to the lower end of a tubular holder **2** by a refractory adhesive **3**. The holder **2** is carried by a protective tubing **4** and detachably connectible to a concentric dual metallic pipe means **5**. The dual metallic pipe means **5** consists of an outer metallic tube **6** and an inner metallic tube **7**, and it is electrically connected to a suitable indicator, e.g., a potentiometer **8**, and mechanically connected to a standard gas source **9**. The dual metallic pipe means **5** connected to the potentiometer **8** and the standard gas source **9** is repeatedly used, together with connecting means therebetween, but the device M illustrated in FIG. 1 consisting of the protective tubing **4**, the tubular holder **2** carrying the ceramic disk **1** and so on are discarded after completing each measurement of the oxygen concentration of molten metal.

A standard gas chamber **10** is formed in the tubular holder **2** so as to cause the standard gas therein to come in contact with the ceramic disk **1** through a porous electrode **11** secured thereto. The porous electrode **11** is made of platinum, silver, nickel, or alloys thereof. For clarity's sake, the electrode **11** is shown in all the figures as separated from the ceramic disk **1**, but it is actually integrally secured to the ceramic disk **1**. One end of a first lead wire **12** is connected to the porous electrode **11**.

The tubular holder **2** of the ceramic disk **1** is secured to one end of the protective tubing **4** by fixture means consisting of a flanged sleeve **13** and refractory adhesive **14**. The refractory adhesive **14** also acts to secure a connector **15** made of synthetic resin material to the protective tubing **4**. The flange portion of the sleeve **13** is buried in the wall of the protective tubing **4** as will be described hereinafter.

The connector **15** is generally of hollow cylindrical shape, and its upper edge fits in the space between the two metallic tubes **6**, **7** of the concentric dual metallic pipe means **5**, as shown in FIG. 1. A central passage **16** is formed through the connector **15** along its central axis, and an inlet pipe **17** is fitted in the passage **16** for communicating the standard gas chamber **10** of the tubular holder **2** with the inside of the inner tube **7**. The connector **15** also has a side passage **18**, in which an outlet pipe **19** is inserted so as to communicate the standard gas chamber **10** with the outside space of the concentric dual metallic pipe means **5**.

The fixture means carries a reference electrode **20**, which is disposed in the outside of the tubular holder **2** with a clearance therefrom. The lower end of a second lead wire **21** is electrically connected to the reference electrode **20**. The first and second lead wires **12** and **21** are gastightly buried in the refractory adhesive **14** and the connector **15** in such a manner that the upper ends of the lead wires **12** and **21** are connected to the inner and outer metallic tubes **7** and **6** of the concentric dual metallic tube means **5**, respectively.

The protective tubing **4** consists of a hollow inner paper cylinder **22**, a refractory mortar layer **23** applied on the outer peripheral surface of the paper cylinder **22** except its upper portion, and an outer paper shell **24** surrounding the outer surface of the mortar layer **23**. The flange of the flanged sleeve **13** is secured to the mortar layer **23** of the protective tubing **4**, as shown in FIG. 1. As a result, the tubular holder **2** carrying the ceramic disk **1** protrudes from the lower end of the protective tubing **4**, and the tubular holder **2** is preferably surrounded by a heat-resistant cap **25** secured to the bottom of the tubing **4**.

The cap **25** is made of a suitable metal or porcelain, and it is provided with two or more holes **26**, which are normally blocked by covers **27**, respectively. The material of the cover **27** for blocking the holes **26** is such that it is carbonized when being dipped in the molten metal to be measured. For instance, the cover **27** is made of at least one of materials selected from the group consisting of paper, cloth, synthetic resin, and leather.

The purpose for blocking the holes **26** of the cap **25** is to prevent slag floating on the molten metal from entering into the inside of the cap **25**. More particularly, when the device M for measuring the oxygen concentration is dipped into the molten metal, the cap **25** penetrates through the slag layer floating on the top surface of the molten metal until it reaches the molten metal to be measured. In the meantime, the covers **27** are carbonized by the heat of the slag and the molten metal, but the carbonizing process of the covers takes a finite time which is long enough for preventing the slag from entering into the space between the tubular holder **2** and the heat-resistant cap **25**. After the carbonized cover is separated from the cap together with slag sticking to the cover, the molten metal enters into the inside of the cap **25**.

The cap **25** also acts to keep the molten metal therein fairly stable or calm even when the molten metal outside the cap is vigorously agitated. With such fairly stable or calm molten metal in the cap **25**, fine particles of slag which are forced into the cap together with the molten metal may come upward and move out of the cap **25** through the holes **26**. Thus, the molten metal in the proximity of the ceramic disk **1** can be kept free from the slag, so that the oxygen concentration of the molten metal per se can accurately be measured in a stable

fashion. Such stabilizing effects of the cap **25** is particularly advantageous for application to refining convertors.

In the preferred embodiment of the invention, as illustrated in FIG. 1, the protective tubing **4** was about 1 meter long, and it was made by forming a 6.5 mm. thick inner paper cylinder **22** with a bias-wound paper layer, applying a 5 mm. thick refractory mortar layer **23** on the outer surface of the paper cylinder **22** with a kneaded mixture of magnesia, silica particles, clay, and water, and forming a 2 mm. thick outer paper shell **24** with another bias-wound paper layer on the outer surface of the mortar layer **23**. It was confirmed by tests that such protective tubing **4** can endure the heat of molten steel at 1,650° C. for about 45 seconds without being burned down, due to its heat-resisting construction and the presence of adiabatic air layers between the mortar layer **23** and paper layers **22**, **24**. Accordingly, a sufficient period of 30 to 35 seconds can be ensured for the measurement of the oxygen concentration of the molten steel by the device M according to the present invention, since 5 to 8 seconds is necessary from the immersion of the device in the molten metal to the beginning of the measurement.

The construction according to the present invention improves the durability of the device for measuring oxygen concentration of molten metal, as compared with that of conventional devices for similar purposes: namely, for instance, a conventional protective tubing consisting of a paper cylinder alone can endure the molten steel at 1,650° C. for only 13 seconds before the paper cylinder is burned down, so that time available for the measurement is at most 7 to 8 seconds; and another conventional protective tubing consisting of an inner paper cylinder and a refractory mortar layer can endure the molten steel at 1,650° C. for only about 30 seconds before the inner paper cylinder is burned down.

The inventors have further confirmed that the durability of the protective tubing in the molten steel at 1,650° C. up to 40 seconds, and the durability in molten steel in a ladle at 1,550° C. up to 50 seconds, by forming the refractory mortar layer **23** with a mixture of alumina particles and aluminum phosphate applied on the bias-wound inner paper cylinder **22**, and enhancing the heat-resistivity and the adiabatic effect of the outer paper shell **24** by impregnating water glass therein. Furthermore, the inventors have succeeded in providing a durability of 50 to 55 seconds in molten steel at 1,650° C. to 1,700° C., by forming the refractory mortar layer **23** with a mixture of silicon carbide, clay, and water, as applied on the bias-wound inner paper cylinder **22**, and enhancing the heat-resisitivity of the outer paper shell **24** by impregnating ethyl silicate therein.

The material for the connector **15**, as shown in FIG. 1, is preferably made of slightly flexible synthetic resin, such as polytetrafluoroethylene, polypropylene, and nylon. When the connector **15** is made of slightly flexible material, it can gastightly engage the lower end of the annular space between the inner pipe **7** and the outer pipe **6** of the concentric dual metallic pipe means **5**. An insulating spacer **28** is inserted between the outer pipe **6** and the inner pipe **7**, so as to electrically insulate the two pipes from each other, as shown in FIG. 1.

The arrangement of the ceramic disk **1** and its tubular holder **2** is not restricted to that as illustrated in FIG. 1. The heat-resistant cap **25** may be dispensed with under certain conditions. More particularly, referring to FIG. 2, the ceramic disk **1** of the aforesaid embodiment may be replaced with a compressed cake of suitable solid electrolyte powders, which cake is directly carried by a tubular holder **2** without using any refractory adhesive. In the figure, an arcuately expanded portion **29** is formed at the lower end of the tubular holder **2**, so as to provide a solid electrolyte chamber **30**, wherein a compressed solid electrolyte cake **31** is fitted by stuffing a powder mixture to it under pressure, which powder mixture is a pulverized solid electrolyte, and the solid electrolyte, for

instance, consists of 85 mol percent of zirconium oxide and 15 mol percent of calcium oxide. A platinum wire **32** is connected to the compressed solid electrolyte cake **31** by inserting the lower end of the wire **32** in the powder mixture when the latter is stuffed to the chamber **30** under pressure. It is important here not to allow the lower edge of the wire **32** to protrude from the cake **31**. In the embodiment of FIG. 2, the platinum wire **32** acts both as the porous electrode **11** and the first lead wire **12** of the preceding embodiment, as shown in FIG. 1. Thus, a separate porous electrode **11** can be dispensed with.

Generally speaking, particles of porcelain materials are sintered when they are heated at a temperature above a certain level, and the sintering tends to reduce the volume of procelain materials. The aforesaid compressed cake **31** is made of those porcelain materials, so that it tends to shrink as it is heated in the molten metal to be measured. In order to compensate for such shrinkage of the compressed cake **31**, the tubular holder **2** is made of special material, such as a heat-resistant glass mainly consisting of quartz, so that volume shrinkage of the solid electrolyte chamber **30** defined by such heat-resistant glass may be greater than the shrinkage of the compressed cake **31** when they are heated in the molten metal. Thus, the cake **31** is gastightly held by its tubular holder **2** in the molten metal. If the tubular holder is, however, made of other material which is less shrinkable than the cake **31**, the gastightness of the joint between the cake **31** and its holder **2** is lost when they are dipped in the molten metal, because the shrinkage of the cake **31** may produce a gap between the cake **31** and the holder **2**. Accordingly, the use of the aforesaid combination of the compressed cake and the tubular holder made of heat-resistant glass will ensure accurate measurement of the oxygen concentration without causing any leakage of the standard gas at the joint of the cake and its holder.

The heat-resistant cap **25** may be dispensed with by directly covering the lower end of the tubular holder **2** and the ceramic disk **1** with the same material as the aforesaid cover **27**, as shown in FIG. 3. In the figure, the lower end of the reference electrode **20** is also enclosed by the cover material **27**. When the tubular holder **2**, as shown in FIG. 3, is dipped in molten metal to be measured, the molten metal reaches the ceramic disk **1** only after the cover material **27** is completely carbonized and separated from the cap. Thus, the ceramic disk **1** is preheated during the period when the cover material **27** is carbonized, so that the ceramic disk **1** is protected from thermal shock caused by immediate contact with the molten metal. Consequently, the risk of the cracking of the ceramic disk **1** by such thermal shock is completely eliminated. The cover material **27** also acts to carry away slag attached thereto, as the cover material **27** per se is carbonized and comes up to the surface of the molten metal. As a result, clean molten metal comes in contact with the ceramic disk **1** and the reference electrode **20**, so as to ensure accurate measurement of the oxygen concentration of the molten metal.

The gastightness of the joint between the ceramic disk **1** and its tubular holder **2** can be improved by applying a suitable protector on the refractory adhesive therebetween. Referring to FIG. 4, a protector ring **33** is applied on the outer surface of the refractory adhesive **3** in such manner that the protector ring **33** bridges the peripheral edge of the ceramic disk **1** and the lower edge of the tubular holder **2** across the adhesive **3** on the side opposite to the standard gas chamber **10**. In the case of measuring the oxygen concentration of molten steel, the protector ring **33** preferably consists of a paste made by kneading tile frit particles or similar glass particles while adding water therein, which particles have a softening temperature of 1,100° C. to 1,400° C. In the case of measuring the oxygen concentration of molten copper, the protector ring **33** may be made by using glass particles having a softening temperature of 700° C. to 900° C. A second protector ring **34** made of glass particles having a softening temperature of 400° C. to 700° C. may be disposed between the refractory adhesive **3** and the aforesaid protector ring **33**, as shown in FIG. 5. In any case, the first protector ring **33** which comes in contact with the molten metal should be made of glass material having a softening temperature lower than the temperature of the molten metal by 100° C. to 400° C.

With the protector ring or rings, as shown in FIGS. 4 and 5, the glass material of such ring or rings is softened when the device M is dipped in the molten metal to be measured, so as to fill up any gaps formed between the cearmic disk **1** and the lower edge of the tubular holder **2**. Thus, the risk of the gas leakage between the standard gas chamber **10** and the molten metal is completely eliminated, for ensuring accurate and reliable measurement of the oxygen concentration. Without such protector ring or rings, the difference of heat expansion between the ceramic disk **1** and its tubular holder **2** may cause minute gaps therebetween, and the molten metal may short-circuit the current path from the reference electrode **20** to the porous electrode **11** through such minute gaps, so as to make the measurement meaningless. The protector ring or rings act to block such minute gaps and prevent the molten metal from short-circuiting the current pass. Thus, the protector ring or rings provide for dependable measurement of the oxygen concentration of molten metal.

In order to collect a specimen of the molten metal from the very spot where the measurement by the ceramic disk **1** is taken, a separate specimen chamber may be formed in the cap **25** of FIG. 1. Referring to FIG. 6, the heat-resistant cap **25** includes an access space **35** defined below the ceramic disk **1** by a pair of partition walls **36** and **37** and a specimen chamber **38** below the access space **35**. The side wall of the access space **35** has at least two holes **39**, and the partition wall **37** between the access space **35** and the specimen chamber **38** has two or more small vertical holes **40** bored therethrough at its central portion. When the device M carrying such cap **25** is dipped in molten metal to be measured, the molten metal may enter into the cap **25** through the holes **26** so as to form an oxygen concentration cell across the ceramic disk **1** in the aforesaid manner. At the same time, the molten metal enters into the access space **35** through the side wall holes **39**, and fills the specimen chamber **38** through the small vertical holes **40** of the partition wall **37**. When the device M is removed from the molten metal upon completion of the oxygen concentration measurement, the device M is likely to be slanted, so that the molten metal in the access space **35** may be split out of the cap **25**, but the molten metal in the specimen chamber **38** may be held there due to the bottle neck formed by the small vertical holes **40** of the partition wall **37**. Thus, the molten metal in the chamber **38** provides a specimen for laboratory analysis.

The construction of the specimen chamber **38** in FIG. 6 is particularly advantageous in providing pure specimen, because the small vertical holes **40** through the partition wall **37** act to prevent the slag from entering the specimen chamber **38**. If an open dipper is used for collecting a specimen, the slag floating on the top surface of the molten metal inevitably enters into the dipper and contaminates the specimen of the molten metal.

In FIG. 6, the upper partition wall **36** of the access space **35** is provided for the following purposes. When the molten metal flows into the specimen chamber **38**, the air is expelled from the chamber **38** through the small vertical holes **40**, and the air may reach the ceramic disk **1** but for the partition wall **36**. Thus, the partition wall **36** is to prevent such air from the specimen chamber **38** from reaching the ceramic disk **1** and affecting the measurement of the oxygen concentration. If high accuracy is not required, the upper partition wall **36** may be dispensed with, as illustrated in the embodiment of FIG. 7.

To illustrate the material and the dimension of the heat-resistant cap **25**, it may be pointed out that the cap **25** of the embodiment of FIGS. 1, 6 and 7 is made by sintering aluminum oxide, inclusive of the partition walls, the access space, and the specimen chamber. Referring to FIGS. 6 and 7, the depth of the specimen chamber **38** was 1.3 cm., and the height of the access space **35** was 0.8 cm., and the diameter of the hole **39** was 0.5 cm., and the diameter of the small hole **40** was 0.3 cm.

Referring to FIG. 8, a specimen chamber may be made separately and attached to the heat-resistant cap **25** of the preceding embodiment. In the figure, a separate specimen chamber **41** is, for instance, made of heat-resistant stainless steel, in a manner similar to the access space **35** and the specimen chamber **38** of FIG. 6. Such separate chamber **41** can be attached to the heat-resistant cap **25** only when a specimen of the molten metal is required for laboratory test. If the measurement of the oxygen concentration alone is sufficient, the separate specimen chamber **41** is not attached to the heat-resistant cap **25**, so that the economy of the measurement and the analysis is improved.

Referring to FIG. 9, it is also possible to form a specimen chamber **38** by enlarging the lower portion of a heat-resistant cap **25**. In the figure, the specimen chamber **38** is formed so as to surround the lower portion of the heat-resistant cap **25**, and the inside of the cap **25** is communicated with the specimen chamber **38** through small holes **42** bored through the lower end of the side wall of the cap **25**. Vent holes **43** are bored on the top wall of the specimen chamber **38** for allowing the air to escape therefrom. The specimen chamber **38** of FIG. 9 is made of mullite.

In order to measure the temperature of the molten metal whose oxygen concentration being measured, a thermocouple (not shown) may be disposed in the proximity of the reference electrode **20** at the outside of the tubular holder **2**, with a suitable clearance from both of the electrode **20** and the holder **2**. The thermocouple is preferably housed in an electrically insulating refractory protective pipe (not shown) made of alumina, mullite, quartz, etc. which protective pipe may be buried in the refractory adhesive **14** of the fixture means so as to extend along the tubular holder **2** substantially to the tip of the holder **2**. Lead wires (not shown) of such thermocouple must be brought to the outside of the device M through the hollow protective tubing **4**, while electrically insulating the leads from the concentric dual metallic tube means **5**, so that the thermocouple may be connected to a suitable temperature indicator (not shown). When the cap **25** is used, the thermocouple should preferably be disposed inside the cap **25** but outside the tubular holder **2**. With such a thermocouple disposed in the proximity of the reference electrode **20**, the temperature of the molten metal is determined while measuring the oxygen concentration thereof, so that the accuracy of the oxygen concentration can further be improved with the knowledge of its temperature.

To protect the cap **25** and the tubular holder **2** during handling and transportation thereof, a suitable protective means (not shown), consisting of a metallic net (not shown) or the like, may be secured to the device M so as to enclose the holder **2** and the cap **25**.

As described in the foregoing disclosure, according to the present invention, a substantially slag-free specimen of the molten metal can be collected from the same spot where the measurement of the oxygen concentration is taken, so that accurate correction of the voltage-oxygen concentation curves may be effected for ensuring reliable measurement of the free oxygen concentration. The accurate determination of the free oxygen concentration provides basis for meaningful comparison of the free oxygen concentration against the total oxygen in the molten metal. The simultaneous determination of the oxygen concentration based on the principle of oxygen concentration cell and collection of the specimen for laboratory analysis simplifies the measuring process of the molten metal.

With the device for measuring the oxygen concentration of molten metal, according to the present invention, the tubular holder of a solid electrolyte can be dipped into the molten metal to be measured without being preheated, while protecting the solid electrolyte from cracking due to the thermal shock and preventing slag from coming in contact with the solid electrolyte. Thus, the gastight joint of the solid electrolyte to its tubular holder is ensured throughout the measurement. Above all, the solid electrolyte can be held in the molten metal for a sufficiently long period of time for ensuring reliable measurement of the oxygen concentration.

Furthermore, the electrical connection of the electrodes of an oxygen concentration cell to an indicator, such as a potentiometer, can easily be accomplished, simultaneously with the mechanical connection of the cell to a standard gas source. A clean specimen of the molten metal can be collected from the same spot where the oxygen concentration is measured, so as to enable the chemical analysis of the very metal whose oxygen concentration is measured by the solid electrolyte.

While several examples have been herein disclosed, it is obvious that various changes can be made without departing from the spirit and scope of the invention as set forth in the appended claims. Further, it is to be understood that all matter hereinbefore set forth is to be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A device for measuring oxygen concentration in molten metal comprising,

an elongated hollow protective tubing,

a pair of spaced concentric metal tubes mounted in and spaced from the inner walls of said protective tubing,

an annular connector element disposed in a gastight manner within the annular space between and at the lower end of said concentric metal tubes,

a tubular holder disposed at the lower end of said protective tubing and in communication with the opening in the lower end of said connector element, and extending below the end of said protective tubing,

a solid electrolyte secured in a gastight manner in the lower end of said tubular holder,

a refractory adhesive for securing said solid electrolyte within said tubular holder, and a layer of glass particles disposed on the outer exposed surface of said refractory adhesive, said glass particles having a softening temperature between about 1,100 and 1,400° C.,

a porous electrode connected to the inner surface of said solid electrolyte and extending into said tubular holder,

a reference electrode extending downwardly from the bottom of said connector element on the outside of said tubular holder and spaced therefrom,

a lead wire connected to each of said porous electrode and said reference electrode and passing upwardly through said connector element and connected respectively to the inner and outer metal tubes of said pair of spaced concentric metal tubes, said connector element being provided with a passage communicating with the upper end of said tubular holder and the space between said protective tubing and said pair of concentric metal tubes, and

means for covering the lower end of said tubular holder and said solid electrolyte, said means including at least one carbonizable material selected from the group consisting of paper, cloth, synthetic resin and leather whereby said carbonizable material is carbonized when the device is introduced into molten metal and rises to the surface of the molten metal with any slag adhering thereto to permit access of clean molten metal to said tubular holder and the outer surface of said solid electrolyte thus increasing

the accuracy of measurement of oxygen concentration in said molten metal.

2. A measuring device as claimed in claim 1 and further comprising a layer of glass particles having a softening temperature between about 400° and 700° C. disposed between said first mentioned layer of glass particles and said solid electrolyte.

3. A measuring device as claimed in claim 1 wherein said covering means consists of carbonizable paper.

4. A measuring device as claimed in claim 1 and further comprising a heat resistant cap secured to the lower end of said protective tubing to enclose the end of said tubular holder extending below the end of said tubing, said heat resistant cap being provided with at least two holes therethrough for admitting molten metal into said cap for contact with said tubular holder and said solid electrolyte, said covering means covering said at least two holes.

5. A measuring device as claimed in claim 4 wherein said heat resistant cap includes a specimen chamber for receiving a specimen of the molten metal when said carbonizable material is carbonized.

6. A device for measuring oxygen concentration in molten metal comprising,

an elongated hollow protective tubing,

a pair of spaced concentric metal tubes mounted in and spaced from the inner walls of said protective tubing,

an annular connector element disposed in a gastight manner within the annular space between and at the lower end of said concentric metal tubes,

a tubular holder disposed at the lower end of said protective tubing and in communication with the opening in the lower end of said connector element, and extending below the end of said protective tubing,

a solid electrolyte secured in a gastight manner in the lower end of said tubular holder, said solid electrolyte being a powder compressed into the form of a cake and the lower end of said tubular holder being provided with an arcuately expanded end portion for receiving and holding said compressed cake of solid electrolyte,

a porous electrode connected to the inner surface of said solid electrolyte and extending into said tubular holder,

a reference electrode extending downwardly from the bottom of said connector element on the outside of said tubular holder and spaced therefrom,

a lead wire connected to each of said porous electrode and said reference electrode and passing upwardly through said connector element and connected respectively to the inner and outer metal tubes of said pair of spaced concentric metal tubes, said connector element being provided with a passage communicating with the upper end of said tubular holder and the space between said protective tubing and said pair of concentric metal tubes, and

means for covering the lower end of said tubular holder and said solid electrolyte, said means including at least one carbonizable material selected from the group consisting of paper, cloth, synthetic resin and leather whereby said carbonizable material is carbonized when the device is introduced into molten metal and rises to the surface of the molten metal with any slag adhering thereto to permit access of clean molten metal to said tubular holder and the outer surface of said solid electrolyte thus increasing the accuracy of measurement of oxygen concentration in said molten metal.

7. A measuring device as claimed in claim 6 wherein said tubular holder consists of quartz glass.

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