May 11, 1971 O. VON KRUSENSTIERNA 3,578,578

MEASURING MEANS FOR MEASURING THE OXYGEN CONTENT IN LIQUID AND GASEOUS MEDIA

Filed Sept. 30, 1968

Fig. 1

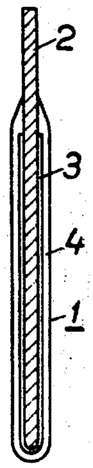


Fig. 2

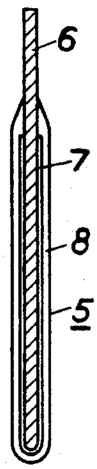


Fig. 3

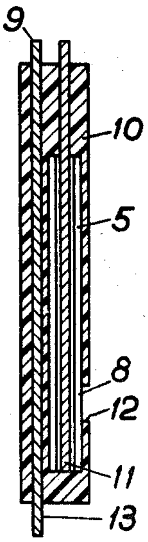


Fig. 4

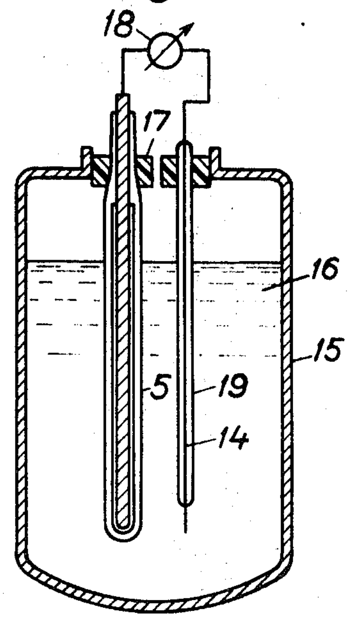


Fig. 5

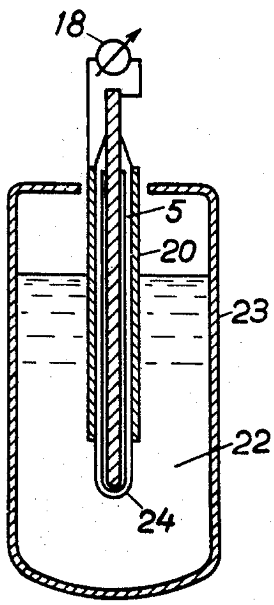


Fig. 6

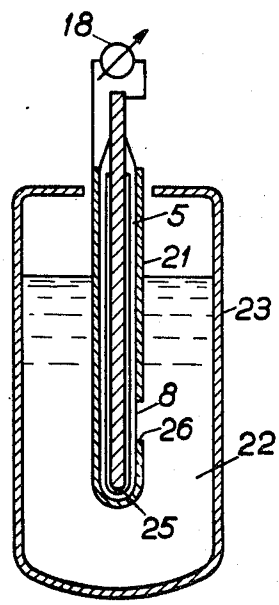
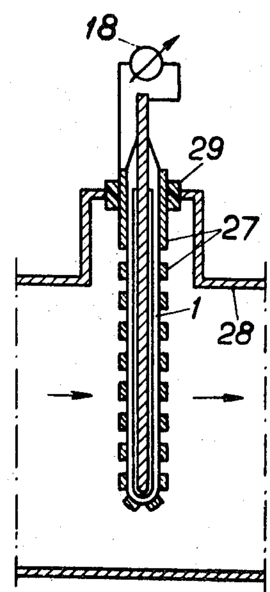


Fig. 7



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1

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MEASURING MEANS FOR MEASURING THE OXYGEN CONTENT IN LIQUID AND GASEOUS MEDIA

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Int. Cl. G01n *27/46*
U.S. Cl. 204—195 10 Claims

ABSTRACT OF THE DISCLOSURE

Measuring means for measuring the exygen content in a liquid or gaseous medium, comprising a solid oxygen ion conducting electrolyte arranged in contact with a reference system having known oxygen potential and consisting of a metal and its oxide which is arranged in contact with a current collector. The current collector is designed as a carrying element for the reference system and the electrolyte which are both arranged as layers on the current collector with the electrolyte outside the reference system.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention relates to the measurement of oxygen content of a liquid or gasseous material.

In the manufacture of steel and when casting steel knowledge of the oxygen content of the steel during the process is of great importance. This is also the case in the manufacture and casting of many metals, for example copper, and many alloys other than steel. With combustion reactions for heating purposes it is often of great importance to be able to determine the oxygen content of the exhaust gases so that the combustion can be regulated for optimum exploitation of the fuel. Thus, in processes of various types, there is a need to be able to effectively determine the oxygen content in a liquid or gaseous medium.

(2) The prior art

One method of determining the oxygen content in a medium is to measure the electromatoric force in an oxygen concentration element having a solid oxygen-ion conducting electrolyte, for example lime-stabilised zirconium dioxide. In previously known means the solid electrolyte of the measuring means normally consists of a relatively thick-walled tube provided with a bottom, on the inside of which is air or a mixture of a metal and its oxide. A platinum wire is often used as current collector. During measuring the outside of the tube is arranged in contact with the medium whose oxygen content is to be measured. In a similar alternative arrangement, also known, the electrolyte is arranged only as a relatively thick-walled bottom while the cylindrical walls consist of an indifferent material.

SUMMARY OF THE INVENTION

According to the present invention it has proved possible to effect a measuring means with which equilibrium is reached in a considerably shorter time than with those described above. The measuring means according to the invention permits measurement of the oxygen content in, for example, metal melts and exhause gases, with a maximum time delay of 3–5 seconds from the moment when the measuring means is inserted in the medium. This provides an essential improvement of the process control

2

for, among other things, steel manufacture, casting and combustion.

The present invention relates to a measuring means for measuring the oxygen content in a liquid or gaseous medium, comprising a solid oxygen ion conducting electrolyte arranged in contact with a reference system having known oxygen potential and consisting of a metal and its oxide, which is arranged in contact with a current collector, characterised in that the current collector is designed as a carrying element for the reference system and the electrolyte which are both arranged as layers on the current collector with the electrolyte outside the reference system.

According to one embodiment of the invention the metal in the reference system may form a continuously coherent unit with the current collector which is then of the same metal and the metal exide may be arranged as a layer on the unit. The surface layer of the body acting as current collector thus serves as the metal in the reference system. According to another embodiment the reference system may consist of a separate layer arranged on the current collector, which is then normally of a different metal from the metal in the current collector, and of a layer of the metal oxide arranged outside this layer, or consist of a layer of a mixture of the metal and the metal oxide.

According to a particularly preferred embodiment of the invention the current collector is in the form of a wire or a rod having a thickness less than 5 mm. preferably less than 3 mm. When a current collector in wire or rod form is used a particularly simple measuring means is obtained which is cheap to manufacture, especially in view of the fact that a wire or rod can be manufactured, for example, with layers of the reference system and electrolyte applied by plasma spraying, in great lengths which can then be cut into shorter lengths suitable for each measuring means to be manufactured from the wire or rod. Whether a current collector having wire or rod shape is used or some other shape, it is advantageous to use a thickness for the current collector less than 5 mm., preferably less than 3 mm., because the measuring means then has little thermal capacity. The layer of the reference system may suitably have a thickness of 0.001–0.5, preferably 0.05–0.3 mm., and the electrolyte layer a thickness of 0.01–0.5 mm., preferably 0.05–0.3 mm.

The necessary counter-electrode may consist of a separate unit which is placed in the medium whose oxygen content is to be determined. It may also be arranged together with the measuring means in a common casing or itself be shaped as a casing around part of the electrolyte layer of the measuring means.

The current collector may consist, for example, of one of the metals nickel, cobalt, iron, chromium, manganese, tungsten, molybdenum, niobium, tantalum or platinum.

The metal in the reference system may consist, for example, of one of the metals, nickel cobalt, iron, chromium, manganise, molybdenum, tungsten, niobium or tantalum.

As an example of suitable material in the electrolyte layer may be mentioned, amongst other things, lime-stabilised zirconium dioxide, which consists of about 85 mole percent $Zr0_2$ and about 15 mole percent Ca0, or other oxygen ion conducting oxides such as yttrium-stabilised thorum oxide which consists of about 92.5 mole percent ThO_2 and about 7.5 mole percent Y_2O_3 and other substances described in Zeitschrift für Chemie, March 1964, volume 3, pages 81–94.

A suitable method of applying the layer of the reference system and the electrolyte is by means of plasma spraying or flame spraying them one after the other on the current collector. It is also possible to immerse the current collector first in a powder mixture of the metal of the reference system and the metal oxide (or only in the metal oxide if the current collector consists of the meta of the reference system) and then to sinter the product thus applied, after which the electrolyte is also applied by the same method in a second step. An alternative method of applying the metal oxide on the current collector if this consists of the metal of the reference system is to oxidize the surface of the current collector so that it becomes coated with an oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further explained by describing a number of embodiments with reference to the accompanying drawing in which

FIG. 1 shows schematically a measuring means according to the invention in which the current collector is of the same metal as the metal in the reference system and forms a continuously coherent unit with the metal in the reference system,

FIG. 2 shows schematically a measuring means according to the invention in which the reference system consists of a mixture of a metal and its oxide,

FIG. 3 shows schematically a measuring means according to the invention which is built together with a counter electrode in an insulating casing,

FIG. 4 shows schematically a measuring means according to the invention arranged together with a separate counter electrode in a space containing a liquid medium,

FIG. 5 shows schematically a measuring means according to the invention, in which a counter electrode is arranged as a casing around a part of the electrolyte layer and which is arranged in a liquid medium,

FIG. 6 is a modification of the arrangement according to FIG. 5, and

FIG. 7 shows schematically a measuring means according to the invention arranged together with a coherent coutner-electrode in a space containing a gaseous medium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The measuring means **1** according to FIG. 1 consists first of a nickel wire **2** having a diameter of 1 mm. and a length of 10 cm. which, for example by being exposed to an oxygen-rich atmosphere, is oxidized on the surface thus forming a layer **3** of nickel oxide which may have a thickness of, for example, about 0.01 mm. The nickel wire acts as current collector and at the same time forms part of the reference system, since the part of the surface layer of the nickel wire which faces the nickel oxide forms, together with the nickel oxide, the reference system of the measuring means. The electrolyte layer consists of a 0.1 mm. thick layer **4** of particles of lime-stabilised zirconium dioxide sintered together and applied by plasma or flame spraying in a conventional manner.

According to FIG. 2 the current collector of the measuring means **5** consists of a 1 mm. thick tungsten wire **6** on which is first applied a reference system consisting of a layer **7** of particles of a mixture of chromium and chromium oxide (Cr_2O_3) sintered together and then a layer **8** of particles of lime-stabilised zirconium dioxide sintered together. The layers **7** and **8** may both be applied by means of plasma spraying or flame spraying.

According to FIG. 3 the measuring means **5** according to FIG. 2 together with the counter electrode **9**, for example a tungsten wire, is arranged in a tubular casing **10** of aluminium oxide or some other heat-resistant insulating material. The lower end **11** of the measuring means is surrounded by the casing and the electrolyte layer **8** is instead exposed at a distance from said end by the arrangement of a window or opening **12** in the casing. The embodiment according to FIG. 3 has advantages, particularly in cases where the measuring means comprises a piece cut from a wire having great length on which the reference system and the electrolyte have been applied. In such cases no reference system layer or electrolyte layer is obtained at the ends after cutting. The ends are protected by the casing **10**. The counter electrode **9** has an exposed end **13** which, like the electrolyte layer **8**, comes into contact with the oxygen-rich medium at the opening when the measuring means is being used.

According to FIG. 4 the measuring means **5** according to FIG. 2, together with the counter electrode **14**, is arranged in a vessel **15** with molten copper **16**. As in FIGS. 5–7 the size of the measuring means and the counter electrode is considerably exaggerated in relation to the size of the vessel. The measuring means and the counter electrode are arranged in a common holder **17** and connected to a high-impedance voltmeter **18** to determine the oxygen content in the molten copper, or to a registering instrument.

The counter electrode **14** may consist, for example, of a molybdenum wire partly surrounded by a potective layer **19**, for example of aluminium oxide.

In the arrangements accoding to FIGS. 5 and 6 the counter electrode is arranged as a tubular casing **20**, **21**, respectively, around a part of the electrolyte layer of the measuring means. At the same time the casing provides a protection for the electrolyte layer of the measuring means. The measuring means and the counter electrode are arranged in a melt of steel **22** in the vessel **23**. As in the arrangement according to FIG. 4 the measuring means and the counter electrode are connected to a voltmeter **18**. They may also be connected to a registering instrument or to a means regulating the supply of components to the melt to influence its oxygen content. In the arrangement according to FIG. 5 the lower part **24** of the measuring means is exposed to be in contact with the melt. In the arrangement according to FIG. 6 said lower part is surrounded by the casing tube **21** and the electrolyte layer **8** is instead exposed at a ditsance from the outer end **25** of the measuring means by the arranegment of a window or opening **26** in the casing tube **21**. The embodiment of the measuring means according to FIG. 6 has the same advantages as those mentioned previously for the arrangement to FIG. 3. If the outer end is exposed before the casing tube is positioned, another insulation from the casing tube can be applied to the outer ends if necessary. In the case exemplified, for example, the casing tube **20**, **21**, respectively, may consist of tungsten or of a metal ceramic material such as a mixture of molybdenum and aluminum oxide. The wall thickness may be, for example, 2 mm.

According to FIG. 7 the measuring means **1** according to FIG. 1, together with the counter electrode **27** joined to this, is arranged in a drum **28** for exhaust gases. The measuring means and counter electrode are insulated from the drum by the insulation **29** and connected to the voltmeter **18** to determine the oxygen content in the exhaust gases. They may also be connected to a registering instrument or to a means influencing valves in conduits for the supply of fuel and air to the space where the combustion takes place. The counter electrode **27** which is in electron-conducting contact with the electrolyte layer may, for example, consist of platinum in the form of a coherent net or a layer with open pores.

I claim:

1. Measuring means for measuring the oxygen content in a liquid or gaseous medium, comprising a current collector, a solid oxygen ion conducting eyectrolyte having an exposed surface and a reference system having known oxygen potential and consisting essentially of a metal and its oxide, in which the current collector constitutes a carrying element for the reference system and the electrolyte which are both arranged as layers on and around the current collector with the reference system in contact with and secured to the current collector and the electrolyte outside and in contact with and secured to the reference system, said current collector comprising a solid wire or rod having a thickness of less than 5 mm, said reference system layer having a thickness of 0.001–0.5 mm., and said electrolyte layer having a thickness of 0.01–0.5mm.

2. Measuring means according to claim **1**, in which the metal in the reference system forms a continuous coherent unit with the current collector which is of the same metal and that the metal oxide is arranged as a layer on the unit.

3. Measuring means according to claim **1**, in which the reference system comprises a separate layer of the metal arranged on the current collector and a layer of metal oxide or a layer of a mixture of the metal and the metal oxide arranged on the current collector.

4. Measuring means according to claim **1**, in which a protective casing is arranged around a part of the electrolyte layer.

5. Measuring means according to claim **4**, in which the protective casing is electrically conducting and constitutes a counter-electrode.

6. Measuring means according to claim **1**, in which the electrolyte layer consists essentially of lime-stabilized zirconium dioxide.

7. Measuring means according to claim **1**, in which the metal of the reference system consists essentially of a metal of the group consisting of nickel, cobalt, iron, chromium manganese, molybdenum, tungsten, niobium and tantalum.

8. Measuring means according to claim **1**, in which the current collector consists essentially of a metal of the group consisting of nickel, cobalt, iron, chromium, manganese, molybdenum, tungsten, niobium and tantalum.

9. Measurisg means according to claim **1**, in which the current collector and the metal in the reference system consist essentially of nickel.

10. Measuring means according to claim **1**, in which the current collector consists essentially of tungsten and the metal in the reference system consists essentially of chromium.

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TA-HSUNG TUNG, Primary Examiner

U.S. Cl. X.R.

136—86, 153; 204—286