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[54] APPARATUS FOR MEASURING IN A CONTINUOUS MANNER OXYGEN IN A MOLTEN METAL

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[52] **U.S. Cl.** .... **204/195 S**
[51] **Int. Cl.** **G01n 27/30,** G01n 27/46
[58] **Field of Search** .... 204/195 S, 1 T; 324/29

[56] **References Cited**

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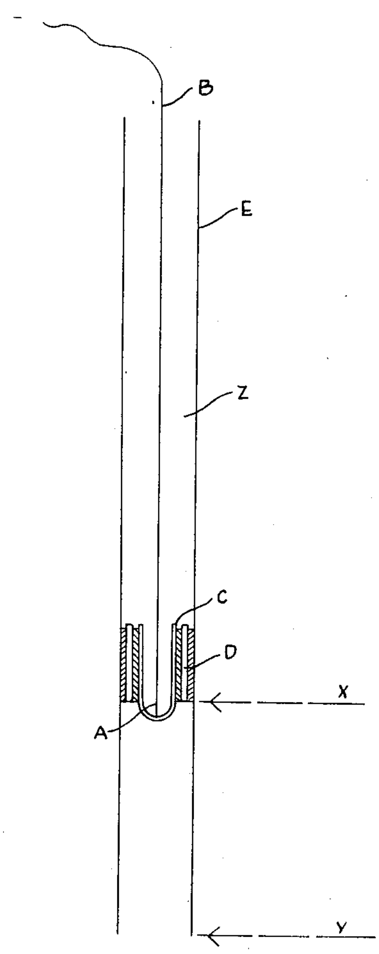
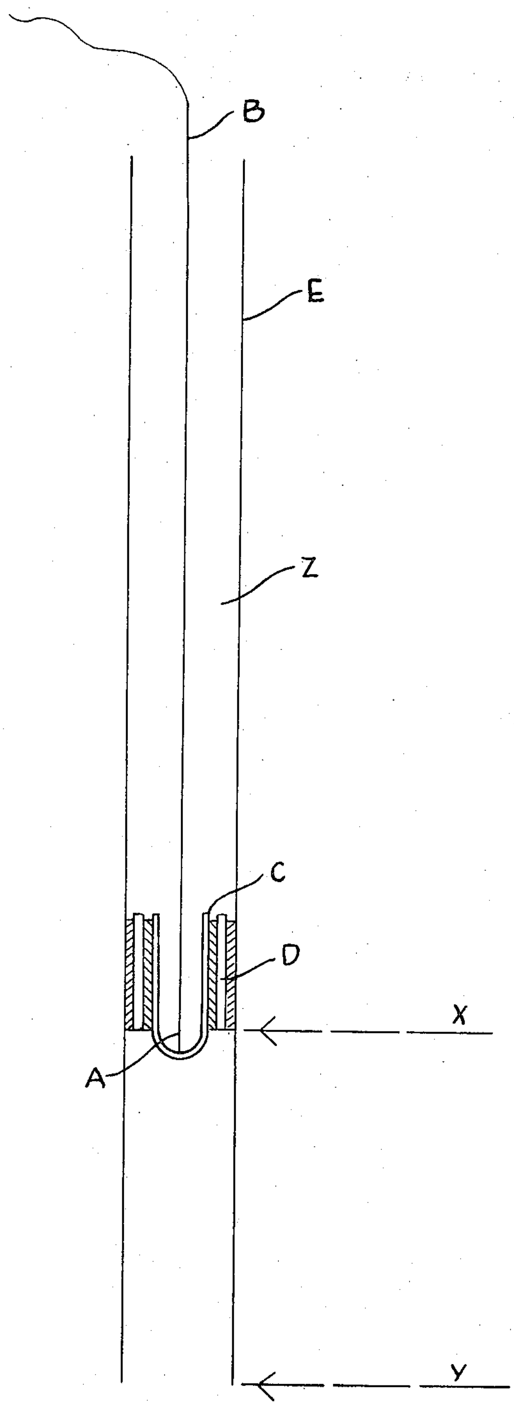
[57] **ABSTRACT**

Apparatus for the continuous measurement of the oxygen contained in a molten metal, comprising means for measuring the electrochemical potential present between two faces of a solid electrolyte, one of these faces being in contact with a controlled oxygen pressure used as a reference and the other being in contact with the metal subjected to test, and an outer tube having a high resistance to mechanical stresses, to thermal shocks and to chemical attack, in which the outer tube is provided at its lower end with an extension in the form of a sleeve, which is designed to be dipped into the liquid metal before the cell is immersed in the said liquid metal so that heat is conducted from the liquid metal to the cell in order to preheat the cell prior to immersion, and to contain a volume of trapped air which is present between the surface of the liquid metal and the solid electrolyte when the cell is dipped in the liquid metal.

15 Claims, 1 Drawing Figure

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APPARATUS FOR MEASURING IN A CONTINUOUS MANNER OXYGEN IN A MOLTEN METAL

Probes designed to measure the oxygen concentration in liquid metals at high temperature by the electromotive force ("emf") method are sometimes defective because they are not strong enough to withstand the mechanical shocks to which they are subjected when handled by workmen and the thermal shocks to which they are subjected when immersed in, and afterwards removed from the bath of liquid metal. Such probes have been described in Luxemburg Pat. Nos. 55,448, 60,630, 60,658 and in British Pat. No. 1,281,718.

A known apparatus for the measurement in a continuous manner of the oxygen contained in a molten metal, such as copper or lead, comprises means for measuring the electrochemical potential present between the two faces of a solid electrolyte, one of these faces being in contact with the controlled oxygen pressure used as a reference, the other face being in contact with the metal under test, an outer tube having a high resistance to mechanical stresses, to thermal shocks, and to chemical attack, and is characterized in that the said tube surrounds the solid electrolyte, is fixed to the solid electrolyte, and forms a contact electrode with the liquid metal.

The solid electrolyte in that known apparatus may be shaped as a rod or strip, held in the end of an outer metal protective tube by means of a cement.

In order to reduce to a minimum the thermal shock to which the refractory parts of the probe and namely the solid electrolyte are subjected at the moment of immersion, it is known to shape the lower end of the outer metal tube so as to have a tongue which extends for a few centimeters, for instance about 7 cm beyond the end of the electrolyte tube. At the beginning of the immersion, the lower end only of this tongue is dipped in the liquid metal and held in that position for a few minutes so that the heat is conducted from the bath to the refractory parts of the probe within the outer metal tube, with the result that these refractory parts are preheated prior to their immersion in the metal.

It has now been found that the preheating is improved when the outer tube is fitted at its lower and with an extension having the form of a sleeve which is designed to be dipped into the liquid metal before immersion of the cell in said liquid metal so that heat is conducted from the liquid metal to the cell in order to preheat the cell prior to immersion, and to contain a volume of trapped air which will be present between the surface of the liquid metal and the solid electrolyte when the cell is dipped in the liquid metal.

The preheating, which is achieved by use of the sleeve, is more uniform and the temperature attained inside the probe is higher than can conveniently be obtained in practice by holding a probe without a sleeve just above the surface of the liquid metal. Experiments have shown that the frequency of cracking of the solid electrolyte at the moment of immersion is strongly reduced by the use of such a sleeve.

Other characteristic features of the invention are described hereinafter and are claimed in the claims.

The accompanying drawing shows a mode of carrying the invention into effect.

In the drawing, A shows an oxygen reference electrode, which consists for example of gas or air or of a mixture of solids and a current conductor B, in contact with a solid electrolyte C, which consists of a tube having a closed end, or a plug or a rod. This solid electrolyte may, for example, consist of zirconia containing lime or yttria in solid solution, so as to conduct electrically the movement of oxygen ions. This solid electrolyte is cemented into a refractory oxide ring D which has a high resistance to the passage of oxygen ions and may consist, for example, of alumina. This refractory oxide ring is then cemented into the metal tube E, which in certain cases may be of mild steel or of alloy steel depending on the corrosive properties of the metal into which the probe is to be immersed.

The lower ends of the tubes C and D are arranged above the lower and of the metal tube E along a distance ranging from 1 to about 5 cm depending on the conditions under which the probe is to be used.

At the beginning of immersion of the probe, air is trapped inside the metal tube between levels X and Y shown in the drawing. At the moment of the immersion the air expands and blows away slag, oxides and other foreign particles which may be present on the surface of the metal. This is an advantage. But more importantly, the trapped air, reduces the thermal shock to which the refractory parts of the level X are subjected.

The length and porosity of the cement column between the tube E and the refractory tube D are sufficient to allow the air to be slowly displaced in the volume at Z by the liquid metal which rises from the level Y to the level X under the influence of the hydrostatic pressure generated by the immersion. The duration of this displacement may advantageously vary between 10 seconds and a few minutes, depending on the porosity and length of the cement column and on the volume of air trapped between X and Y.

If the cement between the tubes E and D is impervious to gas, the gas can have the possibility to escape through a small hole provided in the tube E at the level X, (not illustrated in the drawing).

It has been shown that the oxygen in the air trapped between X and Y has normally little effect on the oxygen content of the metal which comes into contact with the electrolyte tube C, even if all of this oxygen were absorbed by the metal entering the tube D between X and Y.

The tubes of metal or alloy, used for E, may advantageously be used as current conductors between the metal and the recording instrument.

The principal of the air gas trapped illustrated in the drawing may be advantageously applied when the tube E is not a metal or an alloy but any other refractory material such as silica, alumina or silicon carbide.

Many materials such as steel and steel alloys, which may advantageously be used for E react strongly with the oxygen. It has been found that all possible refractory materials which may be used for the tube D and for the cements between the tubes C and D, and between the tubes D and E conduct oxygen ions to some extent, and that an electromotive force ("emf") is produced at high temperatures between E and the reference electrode A. It has been found that this cell gives rise to small stray electromotive forces (stray "emf") which are added to the "emf" produced between the reference electrode and the liquid metal, and which therefore affect disadvantageously the precision of the probe.

It has been found that these stray electromotive forces can be suppressed by incorporating into the cement between the tubes D and E a metal oxide in which the oxygen is held (in the presence of tube E) at a chemical potential approaching the chemical potential of the oxygen in the metal in which the probe is immersed. As to the probe used for measuring oxygen in the liquid copper, for example, finely divided nickel oxide (NiO) may be incorporated into the magnesia cement, either by simple admixture or by forming a solid solution with the magnesis.

What I claim is:

1. Apparatus for the continuous measurement of oxygen contained in a molten metal comprising

a. a cell which comprises:
  i. means for measuring the electrochemical potential present between two faces of a solid oxygen electrolyte:
  ii. one of said two faces being in contact with a controlled oxygen pressure used as a reference; and
  iii. the other of said two faces being adapted to be contacted with the metal which is to be tested;
b. an outer tube having a high resistance to mechanical stresses, to thermal shocks and to chemical attack;
c. said outer tube containing at its lower end a projecting sleeve of high resistance to mechanical stresses, to thermal shocks and to chemical attacks;
d. said projecting sleeve being adapted to be dipped into the liquid metal before the cell is immersed in the liquid metal in order to conduct heat from the liquid metal to the cell and to preheat the cell prior to immersion;
e. said projecting sleeve being adapted to contain a volume of trapped air which is present between the surface of the liquid metal and the solid electrolyte when the cell is dipped into the liquid metal; and being adapted upon immersion to permit expansion of said trapped air to blow away slag, oxides, and other foreign particles which may be present on the surface of the metal being tested, and being adapted to reduce the thermal shock to which the solid electrolyte is subjected; and
f. a column of cement provided between the outer tube and solid electrolyte wherein said cement is gas pervious for allowing said trapped air to be displaced by the hydrostatic pressure of the liquid metal upon immersion, and the porosity and length of the column of cement being adjusted to ensure delay between the immersion and rising of the liquid metal up to said solid electrolyte.

2. The apparatus of claim **1** which further comprises a refractory ring between said outer tube and said electrolyte wherein said refractory ring surrounds the side of said solid electrolyte and wherein said ring is joined to said solid electrolyte and to said outer tube by a refractory cement.

3. The apparatus of claim **2** wherein said refractory ring is alumina.

4. The apparatus of claim **1** wherein cement between said outer tube and said solid electrolyte contains a metal oxide.

5. The apparatus of claim **4** wherein said metal oxide is nickel oxide.

6. The apparatus of claim **1** wherein said solid electrolyte is zirconia containing lime or yttria.

7. The apparatus of claim **1** wherein said outer tube and projecting sleeve are steel.

8. The apparatus of claim **1** wherein said sleeve is about **1** to about **5** centimeters below the bottom of said solid electrolyte.

9. The apparatus of claim **1** which further comprises a hole adapted to enable the trapped air to escape.

10. Apparatus for the continuous measurement of oxygen contained in a molten metal comprising:

a. a cell which comprises
  i. means for measuring the electrochemical potential present between two faces of a solid oxygen electrolyte tube having a closed bottom;
  ii. a reference electrode having known oxygen potential in contact with the inner surface of said tube;
  iii. the outer surface of said tube being adapted to be contacted with the molten metal which is to be tested;
b. an outer tube having a high resistance to mechanical stresses, to thermal shocks, and to chemical attacks;
c. said outer tube containing at its lower end a projecting sleeve of steel;
d. a refractory ring surrounding the sides of said electrolyte tube; and being between said outer tube and said electrolyte tube;
e. said refractory ring being joined to said electrolyte tube and to said outer tube by refractory cement;
f. said projecting sleeve being adapted to be dipped into the liquid metal before the cell is immersed in the liquid metal in order to conduct heat from the liquid metal to the cell and to preheat the cell prior to immersion;
g. said projecting sleeve being adapted to contain a volume of air which is present between the surface of the liquid metal and the solid electrolyte tube when the cell is dipped into said liquid metal; and being adapted upon immersion to permit expansion of said trapped air to blow away slag, oxides, and other foreign particles which may be present on the surface of the metal being tested, and to reduce the thermal shock to which the solid electrolyte tube is subjected; and
h. said refractory cement being gas pervious for allowing said trapped air to be displaced by the hydrostatic pressure of the liquid metal upon immersion, and for ensuring delay between the immersion and rising of the liquid metal up to said solid electrolyte.

11. The apparatus of claim **10** wherein cement between said outer tube and said solid electrolyte contains a metal oxide.

12. The apparatus of claim **11** wherein said metal oxide is nickel oxide.

13. The apparatus of claim **10** wherein said refractory ring is alumina.

14. The apparatus of claim **10** wherein said solid electrolyte is zirconia containing lime or yttria.

15. The apparatus of claim **10** wherein said sleeve is about 1 to about 5 centimeters below the bottom of said solid electrolyte.

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