United States Patent [19]

Jackson

[11] **3,891,512**

[45] **June 24, 1975**

[54] **DETERMINATION OF OXYGEN IN MOLTEN STEEL**

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[73] Assignee: **Ford Motor Company,** Dearborn, Mich.

[22] Filed: **June 24, 1974**

[21] Appl. No.: **482,719**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 312,444, Dec. 6, 1972, abandoned.

[52] **U.S. Cl.** ..... **204/1 T;** 204/195 S

[51] **Int. Cl.**[2] **G01N 27/46**

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

[56] **References Cited**

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G. R. Fitterer, J. of Metals, pp. 92–96, Sept. 1967.

C. K. Russell et al., J. of Metals, pp. 44–47, Nov. 1971.

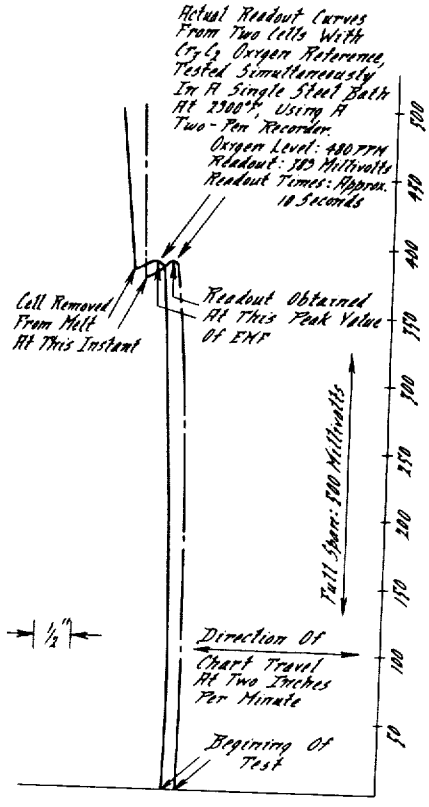
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[57] **ABSTRACT**

Carbides of chromium, niobium, silicon, tantalum and titanium are employed as an oxygen reference material in a rapid process for determining the oxygen content of a molten metal.

3 Claims, 7 Drawing Figures



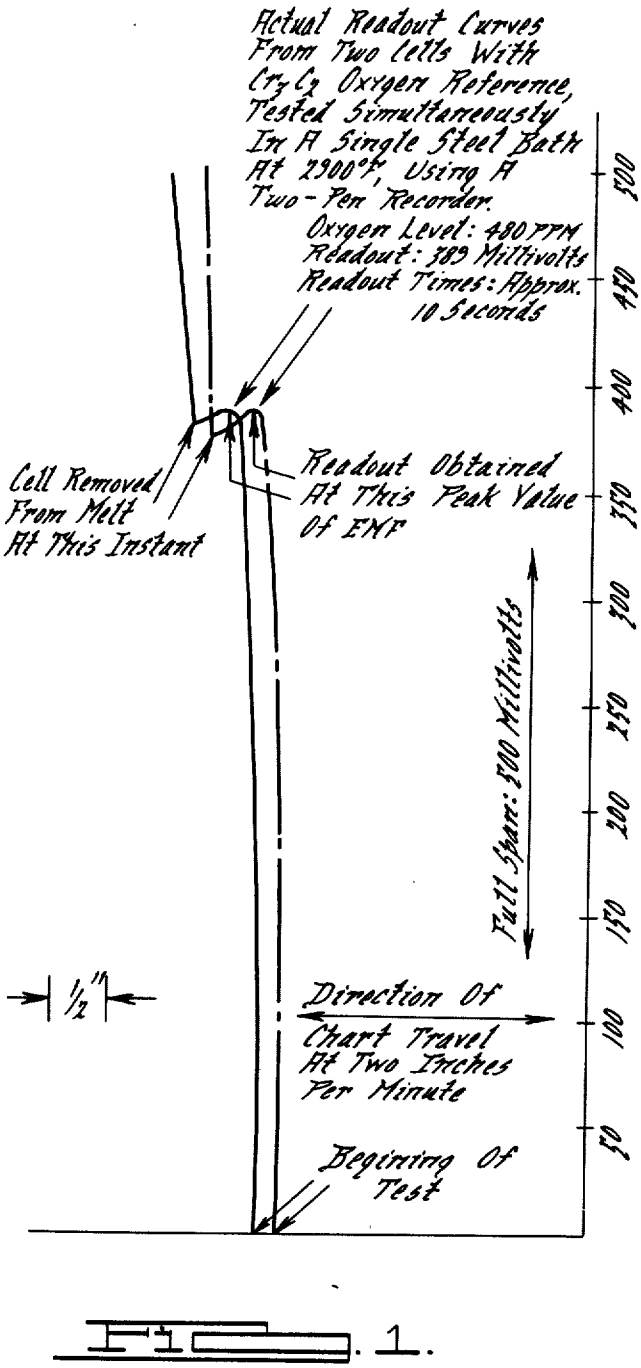


FIG. 1.

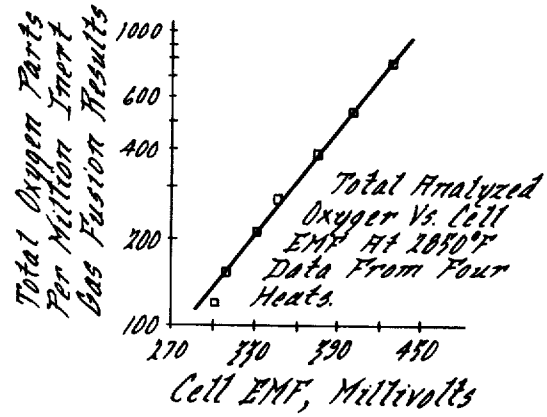


FIG. 2.

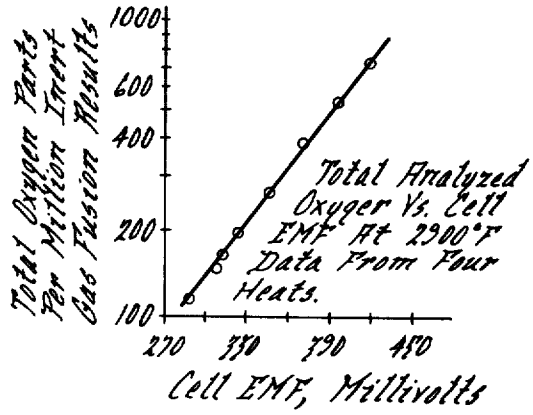


FIG. 3.

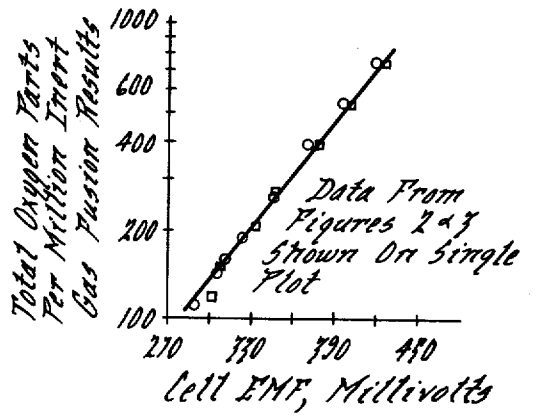
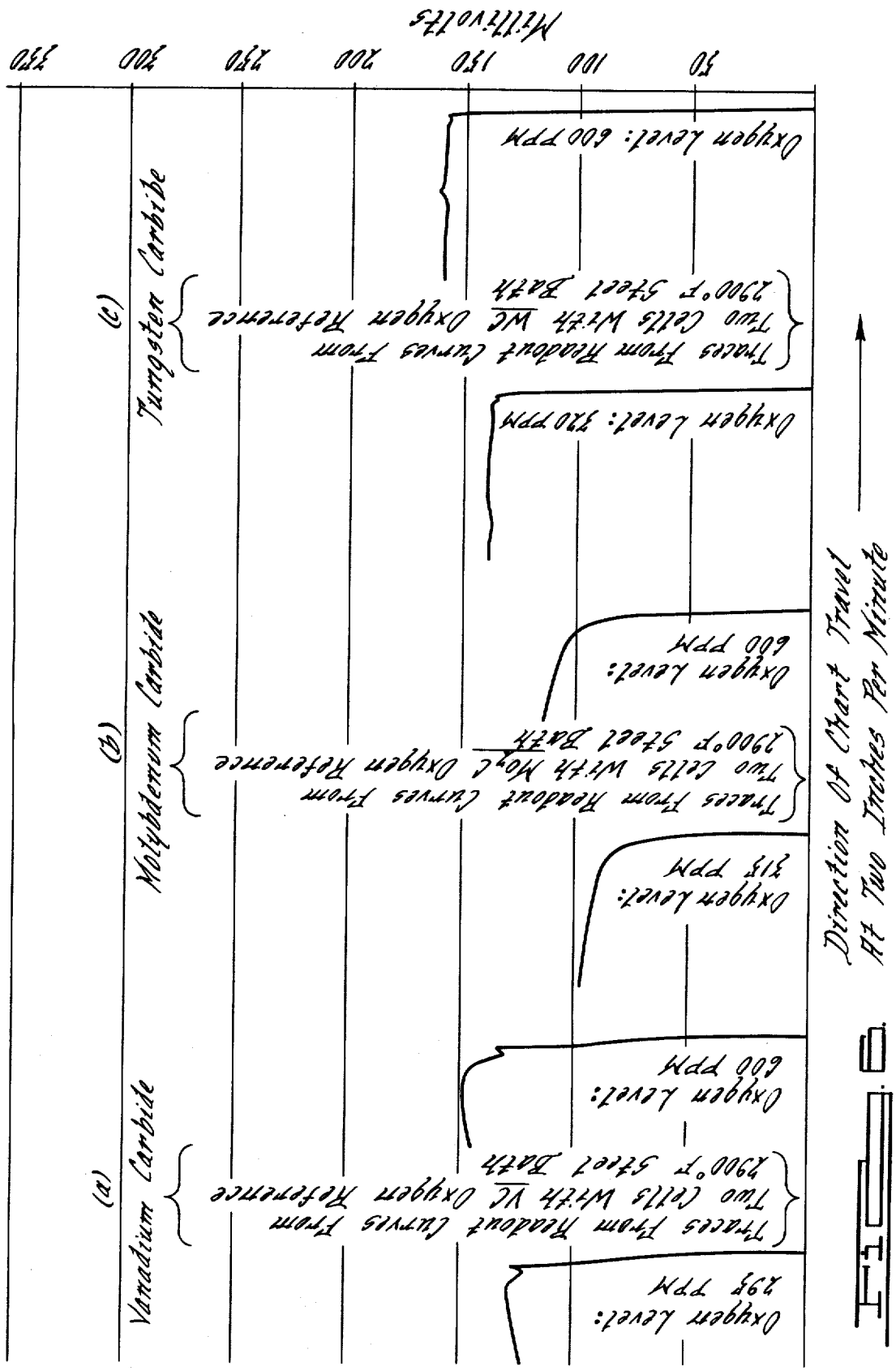


FIG. 4.

Millivolts
50
100
150
200
250
300
350
Direction Of Chart Travel
At Two Inches Per Minute
Oxygen Level: 600 PPM
(a) Zirconium Carbide
Traces From Readout Curves From
Two Cells With ZrC Oxygen Reference
2900°F Steel Bath
Oxygen Level: 208 PPM
Oxygen Level: 600 PPM
(b) Boron Carbide
Traces From Readout Curves From
Two Cells With B4C Oxygen Reference
2900°F Steel Bath
Oxygen Level: 268 PPM
Oxygen Level: 152 PPM
(c) Graphite
Traces From Readout Curves From
Two Cells With Graphite Oxygen Reference
2900°F Steel Bath
Oxygen Level: 248 PPM

Fig. 5


Millivolts
50
100
150
200
250
300
350
(a) Vanadium Carbide
(b) Molybdenum Carbide
(c) Tungsten Carbide
Traces From Readout Curves From Two Cells With VC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 318 PPM
Traces From Readout Curves From Two Cells With Mo_2C Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 730 PPM
Traces From Readout Curves From Two Cells With WC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 293 PPM
Direction Of Chart Travel At Two Inches Per Minute

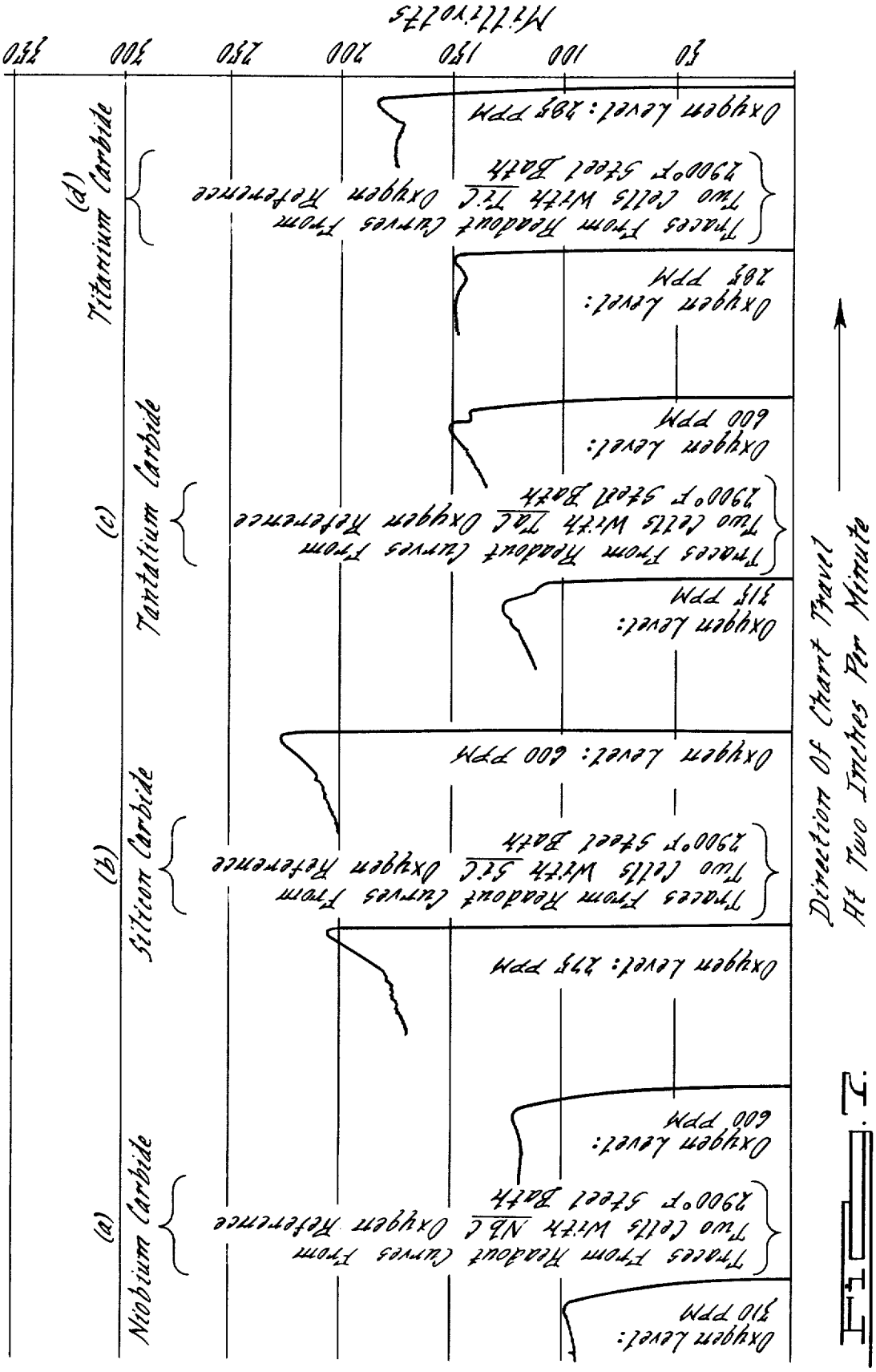

Minutes
50
100
150
200
250
300
350
(a) Niobium Carbide
Traces From Readout Curves From Two Cells With NbC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 310 PPM
(b) Silicon Carbide
Traces From Readout Curves From Two Cells With SiC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 275 PPM
(c) Tantalium Carbide
Traces From Readout Curves From Two Cells With TaC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 600 PPM
Oxygen Level: 285 PPM
(d) Titanium Carbide
Traces From Readout Curves From Two Cells With TiC Oxygen Reference 2900°F Steel Bath
Oxygen Level: 285 PPM
Direction Of Chart Travel At Two Inches Per Minute

FIG. 4

DETERMINATION OF OXYGEN IN MOLTEN STEEL

PREVIOUS APPLICATION

This application is a continuation in part of my previous application Ser. No. 312,444, filed Dec. 6, 1972, now abandoned.

BACKGROUND OF THE INVENTION

The production of a large portion of the steel in this country and abroad is basically a process for reducing the content of carbon and other impurities in a molten bath to a controlled level via injection of elemental oxygen. Both the Open Hearth and Basic Oxygen Furnaces as well as the Electric Furnace are employed for this purpose. Those who operate such facilities are well aware of the difficulty in obtaining molten metal in the teeming ladle with precisely the correct oxygen content. This is true for both killed and rimming grades of steel and critically true for semi-killed steel having optimum balance of the carbon-oxygen product. Great economies could be effected in steelmaking if the precise oxygen content of the steel could be determined essentially instantaneously and economically so that the necessary corrections could be made.

In recent years a great deal of interest has developed in the use of solid electrolyte devices for the purpose of in situ determination of dissolved oxygen in molten steel. Several commercial versions of this concept are now being marketed. These cells are intended for use in very quickly making one single measurement of the oxygen level of the steel, after which they are discarded. These cells are, therefore, contained in disposable devices which house the suitably insulated solid electrolyte together with electrical contact means. Such cells are provided with an internal oxygen reference which has a constant and predictable value for a given temperature. The means for providing such a reference is commonly either a flowing supply of a gas having a definite oxygen pressure, such as air or carbon dioxide, to one face of the solid electrolyte, or provision for location of a mixture of metal/metal-oxide reference material against one face of the solid electrolyte. An example of the first type is described beginning on page 27 in the October 1968 *Journal of Metals* entitled: A Method for Direct Oxygen Determination in Molten Metals, by J. K. Pargeter. Examples of the second type are described beginning on page 22 of the December 1971 *Journal of Metals* entitled: Oxygen Sensor: A New Base for Deoxidation Practices?, by D. A. Dukelow, J. M. Steltzer and G. F. Koons; and beginning on page 1501 of the 1969 Transactions of the Metallurgical Society of AIME. The authors of this paper are Fruehan, Martonik and Turkdogan.

Of the two types described the one which has received the widest acceptance is that which employs a metal/metal-oxide mixture as the oxygen reference material. This is due at least in part to the fact that the disposable portion of the measuring cell can be made a self contained unit with no necessity for an auxiliary supply of gas with the attendant requirements for fittings and connections, and also to the fact that the possibility of gas leakage through the solid electrolyte is greatly reduced. Several metal/metal-oxide systems have been used as reference materials; among them Ni/NiO, Fe/FeO, Cr/Cr_2O_3 and Mo/MoO_3. Cr/Cr_2O_3 has received the widest application in steelmaking oxygen measurements.

It is a disadvantage of solid electrolyte oxygen measuring cells which employ metal/metal-oxide systems as the oxygen reference, that their observed EMF exhibits a marked temperature dependence. The magnitude of this effect is dependent upon the temperature, the level of the oxygen content being measured, the type of solid electrolyte employed and the metal/metal-oxide system used. In many instances a temperature error of ten degrees centigrade can lead to an unacceptably high error in the dissolved oxygen content measurement. The magnitude of this effect is readily amenable to thermodynamic calculation. Such calculations indicate that in a system comprising the commonly used calcia-stabilized-zirconia solid electrolyte and Cr/Cr_2O_3 reference material, for example; that for measurements made in a molten steel bath which contains 800 parts per million dissolved oxygen and in which the temperature is thought to be 1600°C but actually is 1590°C, the error in estimating the oxygen activity from the observed cell EMF will be about 77 parts per million. This combination of temperature level and oxygen content is well within the standard ranges for these two variables which might be encountered in a heat of steel just before tapping, for a low carbon sheet grade. As a result, therefore, of the inaccuracies which may be experienced with this type of cell due to temperature uncertainty it has been necessary to provide either a separate temperature reading or to build a thermocouple into the oxygen measuring cell. Either of these two alternatives adds to the complexity and to the expense of making the oxygen determination and renders the apparatus less viable as a production tool.

SUMMARY OF THE INVENTION

It is readily apparent that if a non-gaseous oxygen reference standard with a low temperature-sensitivity for its oxygen reference pressure could be found, that such a substance would possess great potential for use as an internal standard in oxygen measuring cells for use in liquid metals. This invention is predicated upon the discovery that certain high melting carbides, for example chromium carbide, Cr_3C_2, although they contain no oxygen and therefore cannot generate an oxygen pressure in themselves can nevertheless function to yield an extremely stable and reproducible oxygen pressure reference standard which possesses a greatly diminished temperature dependence for the EMF generated in a solid electrolyte oxygen measuring cell during in situ oxygen determination in molten steel. This novel and unanticipated result does not lend itself to a straightforward concept varification in terms of thermodynamic calculation as in the case of metal/metal-oxide systems because of the paucity of accurate high temperature free energy data for carbides. Nevertheless it may be shown readily be empirical measurements that a very high order of accuracy and reproducibility is inherent in cells constructed with this type of reference material.

It is a benefit of this invention that the temperature coefficient of the EMF in cells so constructed is so small that it is only necessary to know a general temperature *range* in order to use the solid electrolyte cell for an oxygen determination. Uncertainties in the absolute value of the temperature readout which are known to exist between various batches of commercially supplied immersion thermocouples can be ignored out-

right. In fact in most cases oxygen determinations made over the range of 100 to 1000 parts per million dissolved oxygen will not be affected seriously enough to make a practical difference in steelmaking provided that the temperature can be estimated within 20°C (36°F) over the range 1540°C to 1610°C (2804°F to 2930°F).

It is a further benefit of this invention that only very small quantities of the internal standard are required, thus contributing to economical manufacture of the cell.

A characteristic of this invention is that the carbide has a very high melting point and low reactivity toward the solid electrolyte with which it is in intimate contact, thus permitting measurements at very high temperatures.

A further benefit of this invention is that the time-/EMF curve traced by a recording potentiometer, hereinafter referred to as a readout curve, has a single maximum value, rather than an initial value which is not the readout value followed by a trace from which the readout value must be judged; this latter condition is commonly encountered when metal/metal-oxide internal oxygen standards are employed. From the operating steelman's point of view a single-valued readout is an advantage in that it removes a subjective element from the oxygen determination. Typical readout curves obtained with Cr_3C_2 are shown in FIG. **1**, illustrating the excellent speed, curve shape and reproducibility obtainable. These curves may be contrasted with the readout curves shown in the second reference cited above.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates two readout curves obtained using Cr_3C_2 as an oxygen reference material. FIGS. **2, 3** and **4** are semilog plots of test data. FIG. **5** displays the traces from readout curves obtained using zirconium carbide, boron carbide, and graphite as respective oxygen reference materials. FIG. **6** displays the traces from readout curves obtained using vandium carbide, molybdenum carbide, and tungsten carbide as respective oxygen reference materials. FIG. **7** displays the traces from readout curves obtained using niobium carbide, silicon carbide, tantalum carbide, and titanium carbide as respective oxygen reference materials.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Tubular solid electrolytes were prepared as detailed in U.S. Pat. No. 3,674,654. To each of the finished tubes was added approximately 0.2 grams of finely divided Cr_3C_2 powder. Each of these half cells was then completed by inserting a short section of molybdenum wire into the carbide, filling the remainder of the tube with silicon powder, and bonding the powder to form a seal by the addition of a few drops of a 5 percent aqueous solution of NaOH. The molybdenum contact wire projected a short distance beyond the end of the completed half cell.

A number of these units, after drying at 250°F, were then used to measure the oxygen activity in a succession of small laboratory heats of very low carbon steel. For each of these measurements the half cell was held in a metallic clamp by gripping the molybdenum wire, and the solid electrolyte was then immersed into the steel to a depth equivalent to about 90 percent of its length. An electrical circuit to a recording potentiometer of very high impedance was then completed by lead wires to the clamp and to a second separately immersed molybdenum rod. During each of these measurements the steel melt was blanketed with argon to insure a stable oxygen level during the time that the measurement with the cell was in progress. The temperature of the melt was measured with a separate platinum, platinum 10% rhodium immersion thermocouple. The melt temperature was adjusted to a predetermined level for each measurement and was recorded continuously. Samples of the steel were obtained immediately before and after each solid electrolyte EMF measurement of the oxygen activity by solidifying very small specimens of the steel in fused silica tubes.

After each series of measurements, the steel samples were analyzed for total oxygen by the inert gas fusion technique. The values corresponding to each cell measurement were then plotted for each of the melt temperature levels investigated. Examples of the results for temperature levels of 2850°F and 2900°F are shown in FIGS. **2** and **3** to illustrate the excellent reproducibility and correlation with actual oxygen content obtained. These data are shown plotted together in FIG. **4** to illustrate the very smal value of the temperature coefficient of the EMF values.

Although the example shown is for one of the chromium carbides, similar measurements were also made with zirconium carbide, boron carbide, graphite, vanadium carbide, molybdenum carbide, tungsten carbide, niobium carbide, silicon carbide, tantalum carbide, and titanium carbide. Measurements have also been made with ordinary calcia stabilized zirconia as the solid electrolyte. Traces from the individual readout curves obtained with cells using each respective carbide as an oxygen reference material are shown collectively in FIGS. **5, 6** and **7.**

From an examination of these three figures it is immediately obvious that wide variations in readout times, curve shape, and values of the EMF associated with a particular oxygen level are to be expected as different carbides are employed in this way. No pattern of behavior is evident from which one could predict in advance the response of a cell in which a particular carbide was used as an oxygen reference material. In fact, even elements which are adjacent in the periodic table and which form isomorphous carbides may yield dissimilar readout curves.

The above observations on the unpredictable nature of the cell response notwithstanding, the experimental curves may be separated into three general categories. The first such category, shown in FIG. **5**, is for curves which have a shape which is too pointed at the readout value to yield first class accuracy. Materials that fall into this category are zirconium carbide (ZrC), boron carbide (B_4C) and graphite (pure carbon). The very sharp peaks associated with the readout-maxima in these curves tend to be non-reproducible for two reasons. The first reason, which though mechanical in nature is of considerable practical importance, is that recording poteniometers of sufficient ruggedness to withstand continuous service in steel mill environments are not apt to have adequate speed of response to accurately and reproducibly draw such curves. The second reason is that readout curves containing such cusps are more easily altered by slight abberations in the functioning of the cell, whereas a readout value which oc-

curs over a very slightly longer time interval tends to give a more integrated value that is not greatly influenced by very brief fluctuations in cell voltage.

The second category for readout curves, shown in FIG. **6**, includes curve shapes that are unsatisfactory because the carbides produce a response that either reaches no final value in the allowable time period, as is the case with molybdenum carbide (Mo_2C); or reaches no singular peak value, such as with tungsten carbide (WC); or has more than one maximum, as in the case of vanadium carbide (VC).

It will be perceived from these teachings that what is desired is a carbide which, when used as an oxygen reference material in conjunction with a solid electrolyte possessing a high ionic conductivity for oxygen over the temperature ranges and oxygen concentrations commonly encountered in undeoxidized steel during steelmaking, gives a readout within a few seconds, 15 or 20 at the most, which has a single maximum EMF value, and a time-rate-of-response for the EMF developed such that a trace of the readout curve has a rounded shape encompassing the readout level. Of the materials tested for this quality, chromium carbide, Cr_3C_2, is eminently appropriate. Four other carbides which were also found suitable are portrayed by traces of their readout curves in FIG. **7**. They are niobium carbide (NbC), silicon, carbide (SiC), tantalum carbide (TaC) and titanium carbide (TiC).

Attention is here now drawn to the teachings of Tajiri et al. in U.S. Pat. No. 3,403,090. In contrast to the concept of providing a disposable device with a service life measured in seconds, the Tajiri et al invention relates to *continuous* measurement of dissolved oxygen in steel, via a device inserted through the refractory of a melting vessel. Two of the materials used by Tajiri et al. as internal oxygen reference standards were graphite and silicon carbide respectively. The use of these two materials as satisfactory *equivalents* by Tajiri et al., contracts sharply with the findings leading to the instant invention, which determines graphite to be *unacceptable* as an oxygen reference material while silicon carbide is satisfactory. From an examination of FIGS. **1, 5,** 6 and **7** it will be apparent that the peak readout values which are normally obtained with suitable cells within the first few seconds of operation contrast decisively with the generally lower EMF values that are obtained after a longer time period. Although Tajiri does not display traces from readout curves measured from time zero, it is apparent that a continuous readout measurement being recorded over extended time periods would not depend strongly upon an initial high value which occurred within seconds of beginning a reading upon *first* contact with the steel. This is a key point of difference between the teachings of Tajiri et al. and in the instant invention, and it is obvious that the work of Tajiri et al. does not permit a distinction between silicon carbide and graphite with regard to their suitability for use as oxygen reference standards in very rapid single-point measurement of dissolved oxygen in steel via a solid electrolyte technique. Thus the teachings of Tajiri et al. in no way anticipates the use of any of the carbides found satisfactory for application as described herein.

What I claim as my invention is:

1. The process of determining the oxygen content of a molten metal comprising employing in an oxygen activity measuring cell a solid oxygen ion electrolyte; exposing said solid electrolyte on one side to molten metal and on the other to an oxygen reference material having a melting point higher than the melting point of the major component of the metal and which is a carbide selected from the carbides of silicon, titanium, chromium, niobium or tantalum; measuring the electrical potential developed across said solid electrolyte; and reading as a representation of the oxygen content of the molten metal, a single maximum value of the developed potential occurring within no more than 20 seconds after the oxygen activity measuring cell has been exposed to the molten metal.

2. The process described in claim **1** in which the solid electrolyte is selected from the group consisting of thoria, calcia stabilized zirconia, or calcia stabilized zirconia combined with beryllia.

3. The process described in claim **1** in which the molten metal is steel.

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