United States Patent [19]
Wilder

[11] **3,816,269**
[45] **June 11, 1974**

[54] METHOD FOR DETERMINING THE CONCENTRATION OF A METAL IN AN ALLOY MELT

[75] Inventor: **Thomas C. Wilder**, Cambridge, Mass.

[73] Assignee: **Kennecott Copper Corporation**, New York, N.Y.

[22] Filed: **Mar. 28, 1972**

[21] Appl. No.: **238,937**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 31,425, April 14, 1970, abandoned, which is a continuation-in-part of Ser. No. 704,863, Feb. 12, 1968, abandoned.

[52] **U.S. Cl.** .... **204/1 T,** 204/195 S
[51] **Int. Cl.** **G01n 27/46**
[58] **Field of Search** .... 204/1 T, 195 S; 324/29; 23/230 R

[56] **References Cited**

UNITED STATES PATENTS

3,297,551	1/1967	Alcock	204/195 S
3,481,855	12/1969	Kolodney et al.	204/195 S

OTHER PUBLICATIONS

G. R. Fitterer, Journal of Metals Reprint, pp. 1–6, Aug. 1966.

Thomas C. Wilder, Trans. Metallurgical Soc., Aime, Vol. 236, pp. 1,035–1,040, July 1966.

Thomas C. Wilder, Trans. Metallurgical Soc. Aime, Vol. 236, pp. 88–94, Jan. 1966.

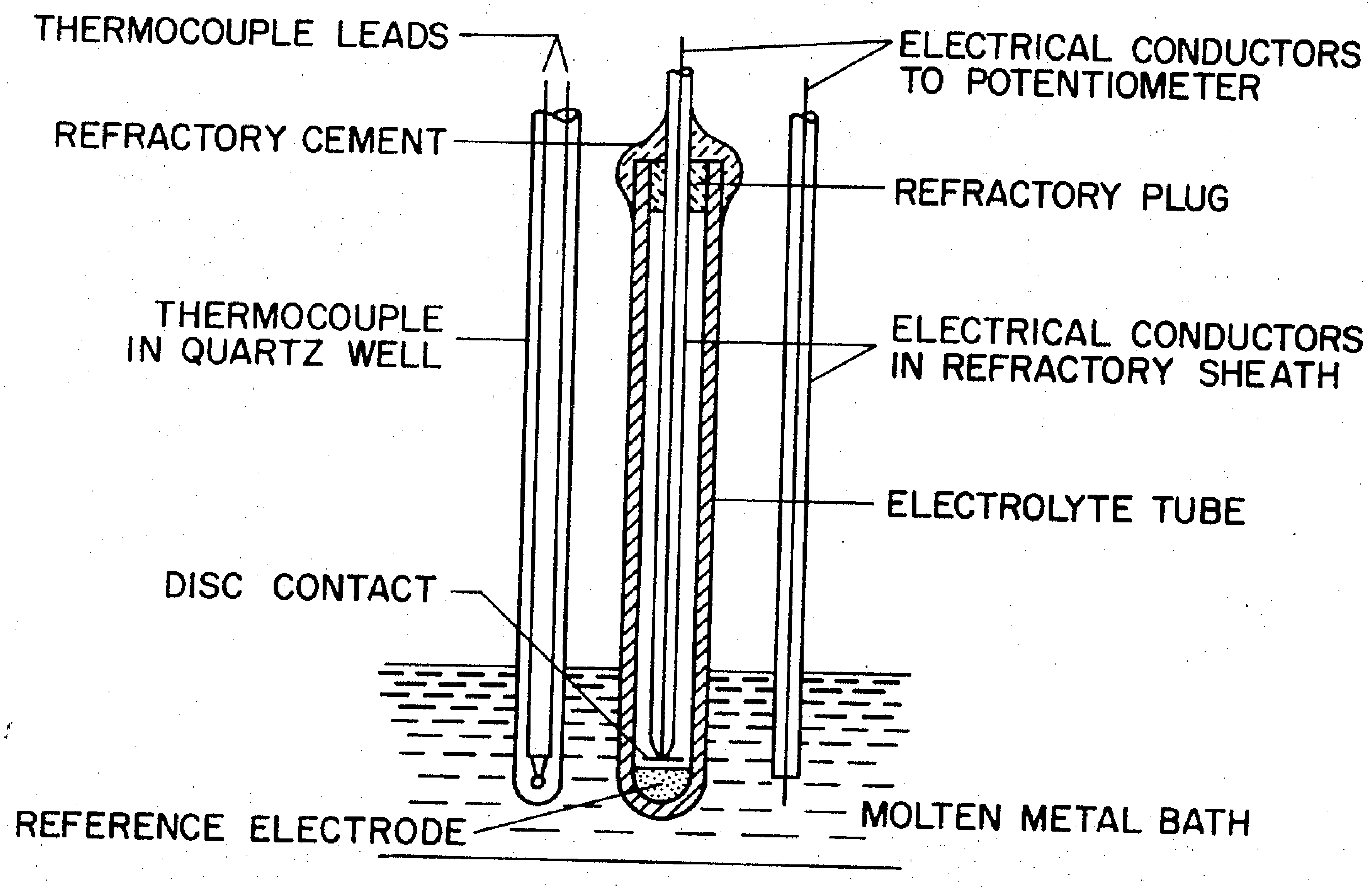
Klaus Schwerdtfeger, Trans. Metallurgical Soc., Aime, Vol. 239, pp. 1,276–1,281 Sept. 1967.

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Lowell H. McCarter; John L. Sniado

[57] ABSTRACT

The method for the direct quantitative measurement of a metal in a molten metal mixture or alloy using a galvanic cell is described.

5 Claims, 2 Drawing Figures



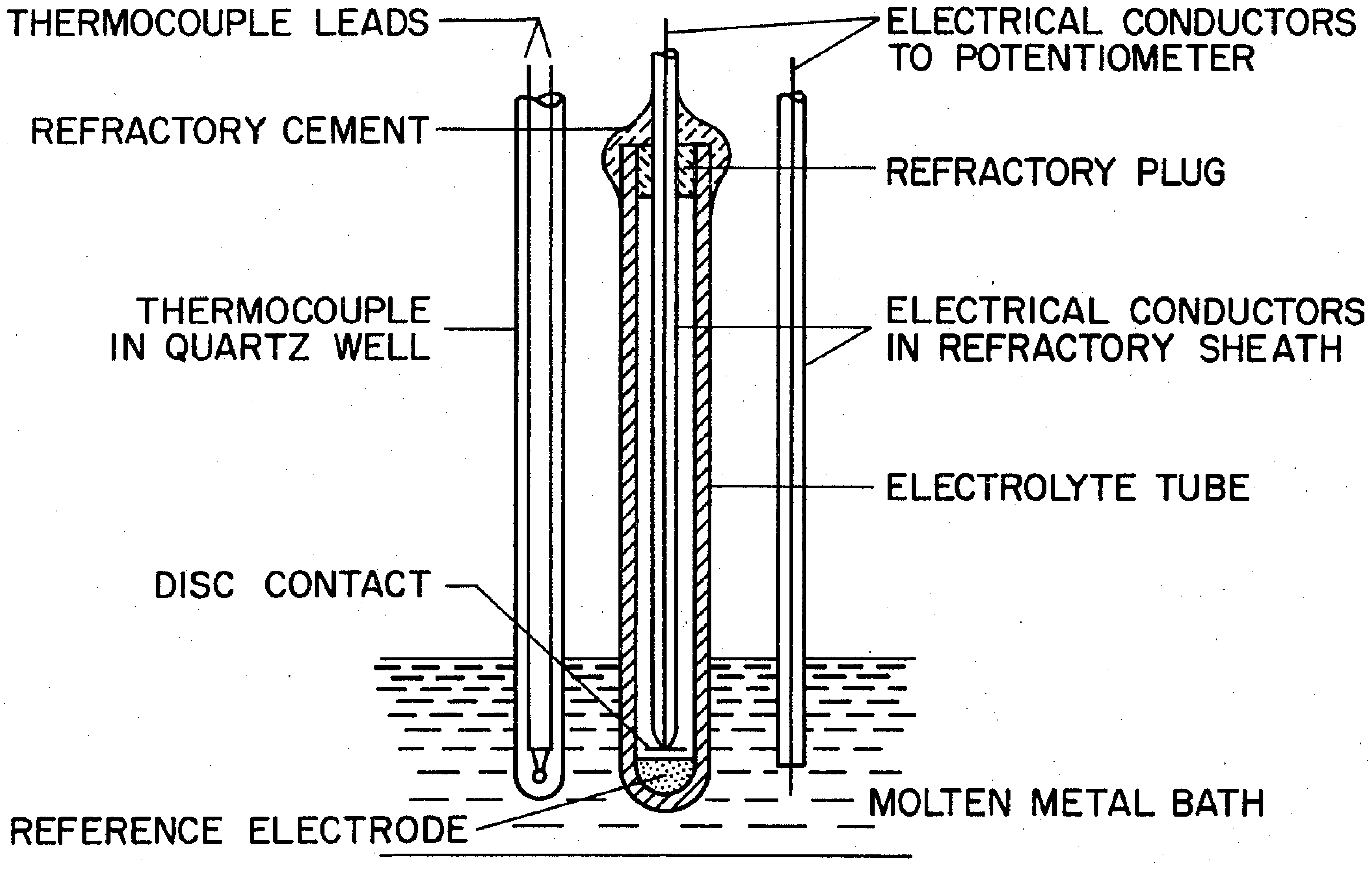


FIGURE I
CELL FOR MEASURING METAL CONCENTRATION IN MOLTEN BATH

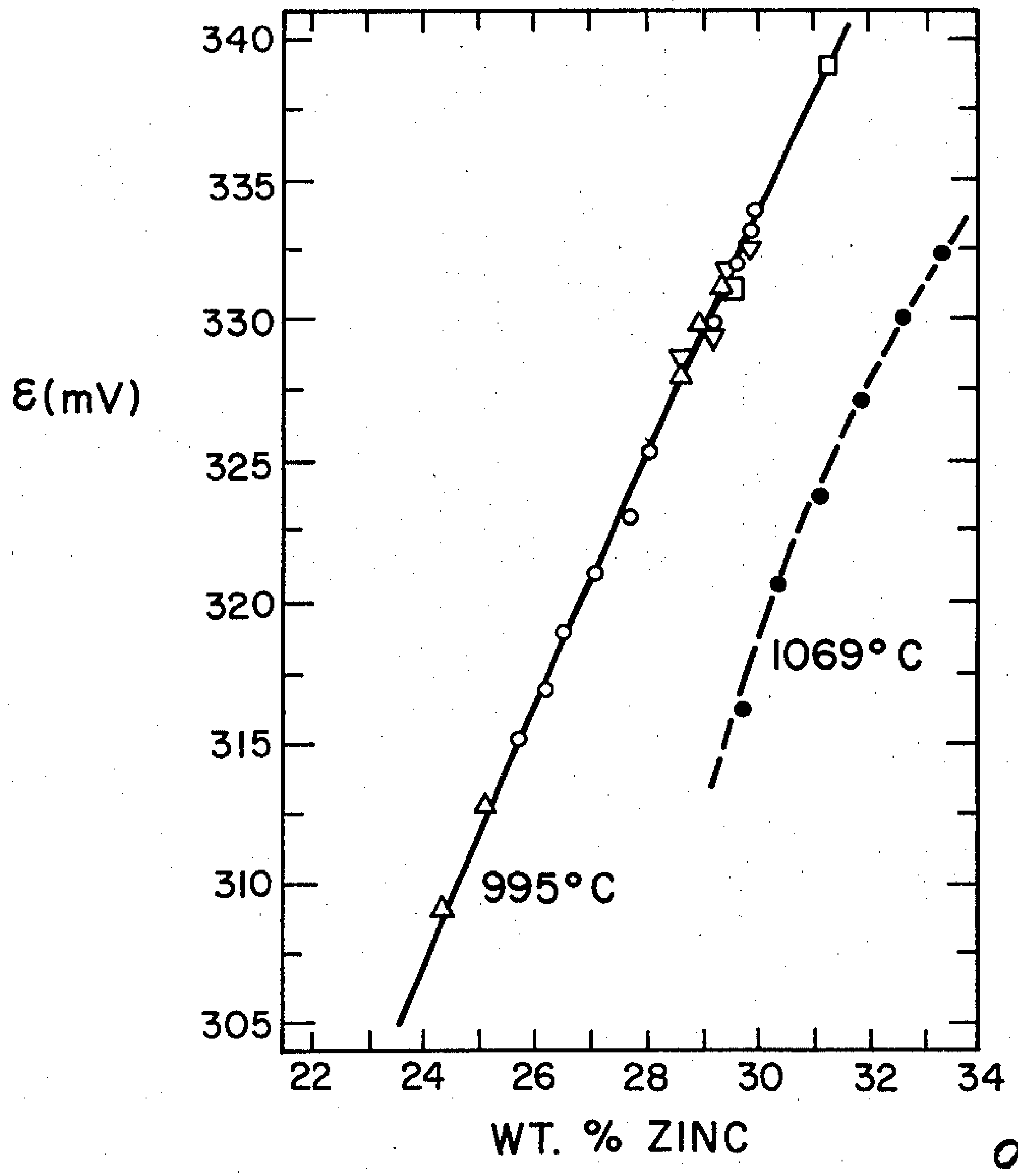


FIGURE 2
EMF OF CELL VS ZINC CONCENTRATION IN MOLTEN BRASS

INVENTOR:
Thomas C. Wilder

BY:
Lowell H. McCarter
HIS ATTORNEY

METHOD FOR DETERMINING THE CONCENTRATION OF A METAL IN AN ALLOY MELT

This application is a continuation-in-part of application Ser. No. 31,425 filed on Apr. 14, 1970 now abandoned which in turn is a continuation-in-part of application Ser. No. 704,863 filed on Feb. 12, 1968 now abandoned.

This invention relates to an electrochemical cell for the determination of the concentration of a metal in molten metal alloy or a mixture of molten metals. The method of this invention is an important tool to the process metallurgist in the preparation of alloys.

Prior to applicant's invention it was not possible to directly determine the concentration of a metal in a molten metal bath. Prior methods required substantial amounts of time to make a quantitative determination of the metal composition. Chemical methods for determining metal concentration in alloys require up to about 30 or more minutes. Spectrographic analysis requires less time but again is not of any real significance to a process metallurgist while a melt is in process.

It is therefore an advantage of this invention that the apparatus and process claimed herein can be used to advantage by a process metallurgist in the working of a molten bath of metal alloys. The process metallurgist may make a determination substantially instantaneous and make the necessary adjustments to the molten bath to bring the metal compositions into the specification range required. This invention will eliminate the errors in adjusting the chemical analysis of a molten metal bath.

It is well known that in the working of a molten metal bath that the most volatile component thereof may leave the bath during the processing. Thus by the time that a wet method chemical analysis or a spectrographic chemical analysis has been performed the composition of the molten metal bath may have changed sufficiently so that the analysis is no longer accurate. The method of this invention gives a quantitative determination for the most chemically reactive metal in a molten metal bath so that the composition of the bath may be adjusted by the addition of a metal or alloy to the desired composition just prior to casting.

It is known, for example, that the oxygen content of liquid metals may be determined using a galvanic cell; see U.S. Pat. No. 3,481,855, M. Kolodney et al; U.S. Pat. No. 3,359,188, W. A. Fischer and U.S. Pat. No. 3,297,551, C. B. Alcock. In these patents the oxygen content must be below the concentration where the oxygen forms an oxide with the solvent metal. Thus if the oxygen content is at the saturation point the EMF is at its minimum reading. Thus the Fischer and Alcock apparatus and methods have limited application.

The literature also contains many references to methods and systems for measuring oxygen content of liquid metals. See, for example, Wilder, T. C., Transactions of the Metallurgical Society of AIME, Vol. 236, July 1966, pp. 1035–1040; Fritterer, G. R., Journal of Metals, Reprint, Aug. 1966, pp. 1–6; Wilder, T. C., Transactions of the Metallurgical Society of AIME, Vol. 236, Jan. 1966, pp. 88–94; and Schwerdtfeger, K., Transactions of the Metallurgical Society of AIME, Vol. 239, Sept. 1967, pp. 1276–1281. The articles all discuss use of galvanic cells for measuring the thermodynamic properties of liquid metal alloys or the oxygen content of metals and alloys. However neither the technical literature nor the patent literature suggest that the concentration of the most chemically reactive metal in a molten alloy can be determined using a galvanic cell. Applicant has, therefore, devised a novel method for measuring the concentration of a metal in a molten alloy using a galvanic cell.

According to the present invention, the concentration of the most chemically reactive metal in a melt of a metal alloy is measured by a method which comprises preparing calibration curves by (1) measuring the electromotive force across a galvanic cell inserted into a molten metal alloy wherein one electrode comprises the molten metal alloy, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as the molten alloy, and the electrolyte is a solid anionic conductor, (2) chemically analyzing samples of the alloy to determine the concentration of the most reactive metal, (3) plotting calibration curves of the measured electromotive force across the cell corresponding to the analyzed concentration of the most reactive metal in the molten alloy, and (4) determining from such curves and a measured electromotive force the concentration of the most chemically reactive metal in a melt of the metal alloy.

The most reactive metal, whose concentration is to be measured, in a melt of an alloy is defined as the metal which has an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal. The process of this invention applies to any alloy system in which this fact is observed. I have specifically found that my method is applicable to the following alloy systems: nickel concentration can be measured in molten copper-nickel alloys, aluminum concentration can be measured in molten aluminum-bronzes, zinc concentration can be measured in molten brasses and chromium concentration can be measured in molten stainless steels. Thus more specifically the invention herein is a method of measuring the concentration of a metal in a melt of an alloy, said metal having an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal of a molten alloy, said molten alloy selected from the group consisting of copper-nickel alloys, aluminum-bronzes, brasses, and stainless steels, which method comprises (1) determining which metal in the alloy has an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal of the molten alloy, (2) measuring the electromotive force across a galvanic cell inserted into the molten alloy, wherein one electrode comprises the molten alloy, the other electrode is a reference electrode comprising a mixture of a metal and its oxide at the same temperature as the molten alloy and the electrolyte is a solid anionic conductor, (3) plotting calibration curves of the measured electromotive force across the cell to correspond to the concentration of the metal having an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal of the molten alloy, and (4) determining from such curves the concentration of the metal in the melt of the alloy.

Determining the metal in an alloy that has an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal can be accomplished by measuring, analyzing or calculating. These three methods are discussed below.

The chemical potential of oxygen in molten copper may be measured by a cell consisting of a solid oxide electrolyte (such as stabilized zirconia), one electrode of known oxygen potential (such as air, pure oxygen, or a mixture of a metal and its oxide), and the other electrode copper containing dissolved oxygen but no other dissolved material. Another method is to pass a gas mixture of known oxygen potential, such as a mixture of CO and CO_2, over molten pure copper for several hours, quench the copper and then analyze for the oxygen content corresponding to that oxygen potential.

The chemical potential of oxygen in oxides may also be calculated from the known free energy of formation of the oxides. The free energy of formation of the oxides are tabulated in many reference sources as a function of temperature. If the free energy of formation of an oxide is unknown it may be determined in the laboratory using a cell consisting of a solid oxide electrolyte, one electrode of known oxygen potential, and the other electrode a mixture of the oxide with its metal. Another method utilizes the measurement of the concentration ratios of an oxidizing and reducing gas, such as H_2O and H_2, which are in equilibrium with an oxide. At equilibrium the oxygen potential of the gas will also be the oxygen potential of the oxide.

A calculation of the type described above follows. This calculation shows that the oxygen potential in zinc oxide is less than that of oxygen normally dissolved in molten copper, so that a cell, such as described herein, when immersed in a molten copper-zinc alloy (i.e., brass) will measure the zinc content of the alloy (i.e., the zinc-zinc oxide equilibrium in molten copper-zinc alloy) and not the overall oxygen content of the alloy.

At 1,200° C the chemical potential of oxygen dissolved in molten copper, a_O (in Cu) has been measured in the laboratory (T. C. Wilder, Trans. Met. Soc. AIME 236, 1966, pp. 1035–1040), and is equal to 0.205 times the oxygen concentration expressed as a mole fraction, X_O, hence:

$$a_O \text{ (in Cu)} = 0.205\ X_O$$

If the oxygen normally dissolved in copper such as molten cathode copper is 10 parts per million by weight, or 0.001 weight percent then

$$a_O = (0.205)\ (0.001)/100 \times 63.54/16 = 8.1 \times 10^{-6}$$

where 63.54 is the atomic weight of copper and 16 the atomic weight of oxygen. Now the free energy of formation of zinc oxide at 1,200° C is –45,860 cal/gfw(C. E. Wicks and F. E. Block, U.S. Bureau of Mines Bulletin No. 605, p. 138) or,

$$\tfrac{1}{2}\ O_2(g) + Zn(g) = ZnO\ (s) \qquad \Delta F^\circ_f = -45{,}860 \text{ cal.}$$

At equilibrium the net free energy change in a system is zero. Thus, by the law of mass action:

$$\Delta F = 0 = \Delta F^\circ_f + RT\ln K$$

$$-45{,}860 + RT\ln\ (1/p_{Zn}\, p_{O_2}{}^{1/2}) = 0$$

In order to determine the chemical potential of oxygen (in this case the partial pressure of oxygen) in zinc oxide, it first must be assumed that the oxide is in equilibrium with pure zinc vapor and thus $p_{Zn} = 1$. Thus:

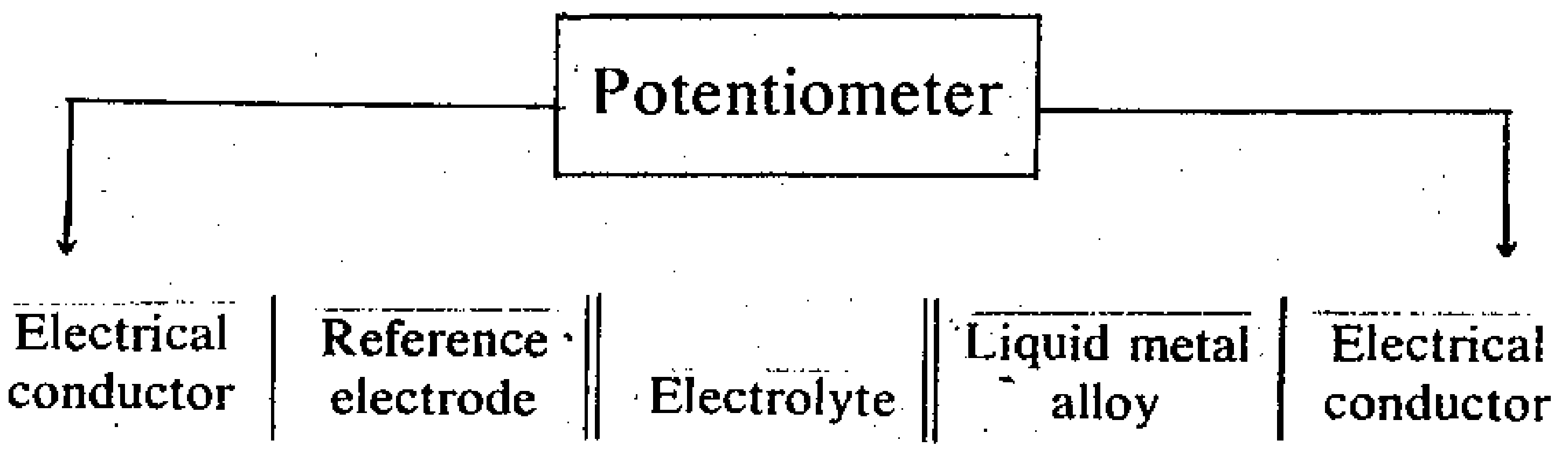
$$-45{,}860 + RT\ln\ (1/p_{O_2}{}^{1/2}) = 0$$

$$-45{,}860 - \tfrac{1}{2}\ RT\ln p_{O_2} = 0$$

$$\bar{P}_{O_2} = 2.24 \times 10^{-14}$$

which is lower than the chemical potential of oxygen normally dissolved in copper at the same temperature. Thus it is clear that the oxygen potential of zinc oxide (2.47×10^{-14}) is lower than the oxygen potential of the oxygen normally dissolved in cathode copper (8.1×10^{-6}). Any new oxygen such as pick-up from air, absorbed by a copper-zinc alloy will, in effect, react with zinc to form ZnO. A cell such as that described herein will show a change in the measured electromotive force caused by the removal of the soluble zinc from the copper-zinc alloy.

The galvanic cell used in measuring the electromotive force may, in general, be represented by



The electromotive force (EMF) of this cell is substantially a simple function of the concentration of the metal to be measured. Thus the potentiometer may be calibrated to give a direct reading of the concentration of the metal in the alloy.

The galvanic or electrochemical cell that can be used for the measurement of the concentration of a metal in an alloy comprises a solid electrolyte and a reference electrode enclosed in the electrolyte. The reference electrode in the solid electrolyte is electrically connected to a potentiometer. An electrical conductor has one end attached to a potentiometer and the other end of the conductor is adapted to be in contact with the liquid metal alloy whose specific metallic concentration is to be measured. The cell is calibrated by determining the electromotive force (EMF) with a given electrode and metal by comparison with chemical analysis of the alloy containing the metal whose concentration is being measured. This data is conveniently correlated in a table or family of curves with parameters of metal concentration and electromotive force (EMF).

The cell and process of this invention can be used for measuring the concentration of the most active metal in the alloy compositions provided that the oxygen potential of the metal's oxide is less than the activity of the oxygen normally dissolved in the solvent metal. In other words, the invention embraces the measurement of the most chemically reactive metal in a molten alloy providing enough oxygen is present to cause the formation of small amounts of that metal's oxide. Specific examples of metal concentrations that can be measured in molten engineering alloys include nickel in copper-nickel alloys, aluminum in aluminum-bronzes, chromium in stainless steels and zinc in brasses. These alloys are given as specific examples but are not to be considered as limiting the scope of this invention except as defined in the appended claims.

The applicant has discovered that the chemical thermodynamic activity of the most active metal in a molten alloy makes it possible to determine the concentration of the most chemically reactive metal in the alloy by measuring the EMF across a galvanic cell and calibrating it so that the measured EMF corresponds to the metal concentration. The residual oxygen in the molten alloy forms an oxide with the most chemically reactive metal. In the case of brass, as determined by available thermodynamic data, the residual oxygen must be substantially less than 1 part per million, i.e., about 0.005 ppm, before a separate phase of zinc oxide will not form.

The theory of the invention will be explained as applied to the brass system where a nickel-nickel oxide reference electrode is used. However it is to be understood that this theory is presented by way of explanation. It is not considered to be limiting except as defined in the appended claims. In the brass system the zinc forms a zinc oxide phase with whatever residual oxygen may be in the metal. Since zinc oxide forms in the Cu-Zn-O system with less than one ppm oxygen in the molten alloy the EMF measurement is not measuring the oxygen content of the molten metal.

By way of further explanation of how this cell functions, the reaction which occurs when the circuit of the cell is closed is:

$$\mathrm{Zn\ (in\ Cu)} + \mathrm{NiO}(s) = \mathrm{ZnO}(s) + \mathrm{Ni}(s) \qquad (1)$$

The free energy of this reaction, and the electromotive force related thereto is given by:

$$\Delta F = -2F\epsilon = \Delta F^{\circ}_{f}\,(\mathrm{ZnO}) - \Delta F^{\circ}_{f}(\mathrm{NiO}) - RT\ln a_{Zn} \qquad (2)$$

where F is the Faraday equivalent (23,063 cal/volt eq.) ϵ is the electromotive force of the cell in volts, ΔF°_{f} (ZnO) and ΔF°_{f} (NiO) are the standard molar free energies of formation of ZnO and NiO respectively, R is the universal gas constant, T is the absolute temperature in degrees Kelvin, and a_{z_n}, is the thermodynamic activity of zinc in the molten copper-zinc alloy. At constant temperature, all the terms in equation 2 are constant except ϵ and a_{z_n}. The latter term is directly related to the concentration of zinc in the alloy; hence the value of ϵ is directly related to the concentration of zinc in the alloy.

The reason that zinc oxide (ZnO) must exist in the brass is explained as follows. The standard molar free energy of formation of ZnO, and the molar free energy of oxygen in ZnO at 995° C is about −51,500 cal/mole. The molar free energy of oxygen in solution with copper at 995° C is about $-6390 + 5825 \log X_O$, where X_O is the mole fraction of oxygen in copper. At the point where the molar free energy of oxygen in copper is equal to that in ZnO (obtained by equating −51,500 and $-6390 + 5825 \log X_O$), X_O is 1.8×10^{-8} which converts to 0.005 parts per million of oxygen. At any concentration of oxygen in molten brass in excess of this infinitesimal amount, ZnO must exist as a separate discreet phase in the system, and the only reaction which can occur is the one shown in equation 1. A substantially similar calculation may be made to show that a vanishingly small amount, i.e., less than about 1 ppm, of oxygen is required to form Al_2O_3 from molten aluminum bronzes, or Cr_2O_3 from molten stainless steels.

The ability to measure the concentration of a metal in a molten alloy as described arises from the phenomenon that most of the oxygen in the alloy systems is in the form of a solid metal oxide, i.e., MeO(s) (where Me is the metal whose concentration is to be measured) and that the electromotive force of the cell is a function of the Me-MeO (metal-metal oxide) equilibrium wherein the metal, Me is not at unit activity but dissolved in the alloy. Therefore the process can be used to measure the metal concentration in any alloy system in which the most active metal forms a separate oxide phase before the overall oxygen content is larger than would be desired in the alloy.

Using the method of analysis as described above with reference to the copper-zinc system, the applicant has determined that nickel is the most chemically reactive metal in copper-nickel molten alloys, aluminum is the most chemically reactive in aluminum-bronzes molten alloys (may contain in addition to copper and aluminum such elements as iron, nickel and manganese), and chromium is the most chemically reactive in stainless steels.

Having determined, by one of the three methods discussed above, the most chemically reactive metal in the molten alloy bath at the melt temperature the next step is to prepare calibration curves. FIG. 2 contains calibration curves at two melt temperatures for determining the concentration of zinc in molten brass. A series of electromotive force readings was taken and a sample of the alloy for chemical analysis was withdrawn from the melt. The composition of the melt was then changed either by allowing the most volatile metal component to vaporize from the melt, as zinc in the molten brass, or by adding weighed amounts of a pure metallic component to the melt. Then another series of electromotive force readings was taken and another sample of the alloy was withdrawn from the melt. These steps were repeated until a sufficient number of electromotive force readings and alloy sample chemical analyses have been made to give data for preparing the calibration curves. It is particularly advantageous to prepare calibration curves for each alloy at a number of different temperatures. Interpolations can then be made when the melt temperature does not correspond to one of the calibration curves.

Any of a number of different electrolytes may be used within the scope of this invention. However the electrolyte must be characterized as being primarily an anionic conductor. The electrolytes are those that allow the movement of oxide ion vacancies under the influence of an oxygen potential gradient. The electrolyte must not be porous to the extent that a metal or its alloy penetrate the electrolyte to the degree that would cause a short circuit.

Any electrolyte that meets the aforementioned characteristics may be used within the scope of this invention. The electrolyte generally consists of a host material and a dopant material to a minor extent, i.e., from about 5 to 25 percent dopant. The dopant dissolves in the host material causing the host material to have a number of anionic vacancies. This results in an electrolyte as being primarily an anionic conductor. The electrical conduction is by the movement of oxide ion vacancies. Suitable electrolyte host materials include the oxides of thorium and zirconium, to which an oxide of the alkaline earths or rare earths, e.g., calcium oxide or yttria have been added to form a solid solution. The host material, e.g., thoria or zirconia, and the dopant, e.g., calcium oxide, are mixed in the desired proportions and cast into the shape of the desired electrolyte, for example a closed-end tube or crucible. The preferred electrolyte is a calcia stabilized zirconia containing about 92.5 percent zirconia and about 7½ percent calcium oxide. This calcia stabilized zirconia is commercially available under the trade name of "ZIRCOA."

Enclosed in the electrolyte is a reference electrode material. A gas or mixture of gases of known oxygen potential may be used as the reference electrode. The preferred gas is oxygen. Suggested mixtures of gases include air, carbon monoxide and carbon dioxide, and hydrogen and water vapor. However the preferred reference electrode is a metal in admixture with its oxide. Specific examples of these reference-electrodes include a mixture of iron and iron oxide, chromium and chromium oxide, copper and copper oxide, nickel and nickel oxide, titanium and titanium oxide and molybdenum and molybdenum oxide. Any mixture of a metal and its oxide that is a solid at the melt temperatures and has relatively stable thermodynamic properties may be used as the reference electrode. Generally the reference electrode will contain about equal portions of the metal and the metal oxide.

The reference electrode may be prepared by mixing equal volumes of screened and sized metal and metal oxide powders. The powders are thoroughly blended in a rotary mixer or the like. The mixed metal and metal oxide powders are compressed and sintered in the electrolyte tube. Contact to the metal/metal oxide sintered pellet may be made by a platinum disc spot welded to a platinum wire or other electrical conductor. The platinum wire or electrical conductor may be sheathed in a protective tube of quartz, alumina or the like so that mechanical pressure may be applied to the platinum disc.

Contact to the molten metal bath is made with an electrical conductor sheathed in a quartz, alumina, or the like, protective tube. The molten metal bath contact electrical conductor is selected so that it is not dissolved or corroded by the molten metal bath.

Because of the relative sensitivity of the measurements required in this invention it is preferred to use platinum leads from the reference electrode in the electrolyte to the potentiometer and an electrical conductor from the molten bath to the potentiometer selected so that it is not attacked by the molten metal bath. Specific examples of electrical conductors from a brass melt to the potentiometer are tantalum, tungsten, rhenium, molybdenum and the alloys thereof.

The reproducibility of the cell potential for most alloy systems is excellent. It is also very sensitive to slight composition changes. Owing partly to the low electrical resistivity of the electrolyte, cell potential may be resolved to the nearest 0.1 millivolt. This means that a composition change of 0.02 weight percent can be detected if the temperature is accurately known. Thus if the temperature in the area of the melt containing the cell is known to ± 2° C. the metal concentration can be determined with a range narrow enough to meet most requirements of the process metallurgist.

FIG. **1** shows pictorially a preferred embodiment of the electrochemical cell of this invention in a molten metal bath.

FIG. **2** graphically presents the electromotive force of a cell as a function of zinc concentration in molten brass.

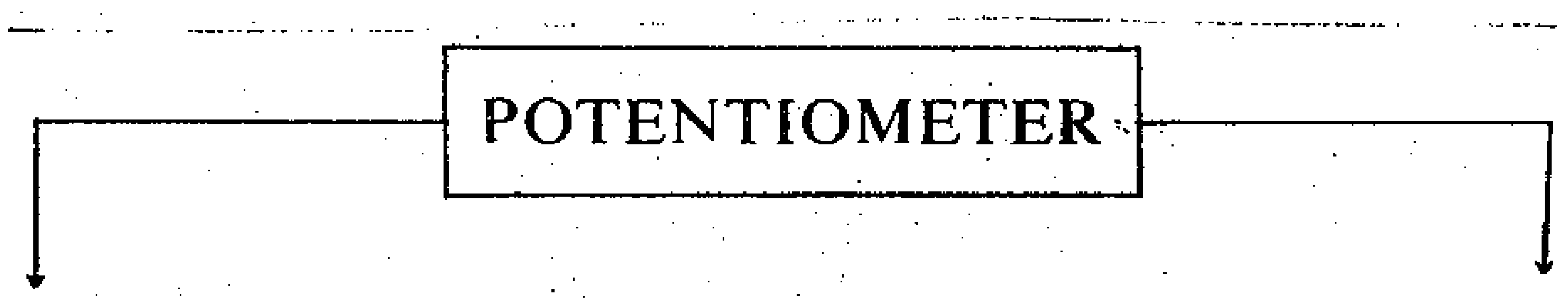
EXAMPLE 1

This example illustrates an electrochemical cell in accordance with this invention as it is used to directly measure the zinc content of molten copper-zinc alloys.

The internal cell arrangement was essentially that shown in FIG. **1.** The electrochemical cell consisted of an electrolyte in the form of closed-end elongated hollow body preferably having a tubular configuration formed from zirconium oxide containing about 7½ weight percent calcium oxide. Equal volumes of screened and sized (−250 mesh) nickel and nickel oxide powders were thoroughly blended, compressed and sintered in the electrolyte to form a nickel/nickel oxide pellet reference electrode. Contact to the nickel/nickel oxide pellet was made by a platinum disc spot welded to a platinum wire. The platinum wire was sheathed in a quartz tube so that mechanical pressure could be applied to the platinum disc. Contact to the molten copper-zinc bath was made by a tantalum wire sheathed in alumina. A tantalum contact was chosen since it does not dissolve in the molten copper-zinc alloy.

Alumina cement was used to seal off the interior of the electrolyte body from condensing zinc vapor contamination. A thermocouple in a quartz well was provided to give accurate temperature measurements in the region of the electrolyte and the molten copper-zinc alloy contact.

This electrochemical cell may be represented as



$$\text{Pt} \mid \text{Ni, NiO} \parallel ZrO_2 + 7\tfrac{1}{2}\%\text{CaO} \parallel \text{Zn(inCu), ZnO} \mid \text{Ta}$$

The internal cell similar to that shown in FIG. **1** was placed in an alumina crucible adapted to be heated in a resistance furnace. The brass (249 grams, 30 percent zinc) whose zinc concentration was to be measured was charged to the crucible and melted. The composition of the alloy was changed by either allowing the zinc to vaporize from the melt, or by adding weighed amounts of pure copper. The zinc oxide present in the copper-zinc melt, as shown in the cell above resulted from the reaction of zinc with trace amounts of oxygen present in the atmosphere above the melt. In all cases samples were taken correspondingly to each reading and a chemical analysis was made. Readings were taken for various alloy compositions at 995° C and 1,069° C.

Cell potentials were measured with a null potentiometer. The data obtained are shown in the Table and plotted with the parameters of zinc concentration and EMF as shown in FIG. **2.**

The reproducibility of the cell potential was excellent and was very sensitive to slight composition changes. Cell potentials were easily resolved to the nearest 0.1 mV. This meant that a composition change of 0.02 weight percent zinc could be detected if the temperature is accurately known. Thus if the temperature in the area of the melt containing the electrochemical cell is known to ± 2° C then the melt's composition can be determined to ± 0.06 weight percent zinc.

TABLE

Potentials of Cell as Function of Zinc Concentration in Molten Brass

Alloy No.	at 995° C Wt. Pct. Zn	EMF of Cell, mV
1	24.38	309.2
2	25.18	312.8
3	25.72	315.0
4	26.21	316.9
5	26.54	319.0
6	27.15	320.9
7	27.70	323.1
8	28.03	325.5
9	28.68	328.1
10	28.72	327.7
11	29.06	329.8
12	29.09	329.9
13	29.10	329.6
14	29.52	331.3
15	29.56	331.3
16	29.60	331.3
17	29.68	332.0
18	29.82	332.5
19	29.92	334.0
20	29.94	333.1
21	31.32	339.0
at 1069° C		
22	29.76	316.0
23	30.37	320.6
24	31.11	323.7
25	31.89	327.2
26	32.71	330.1
27	33.45	332.3

EXAMPLE 2

This example illustrates that the galvanic cell and process of this invention may be used to measure the concentration of a metal in a molten metal alloy when the metal to be measured is at relatively high and low concentrations.

A. Using essentially the same cell arrangement as described in Example 1 EMF readings in millivolts were obtained on a molten copper-zinc alloy held at 798° C where the zinc concentration was from about 69.5% to 94.4%. The results are tabulated below:

Alloy No.	Wt. Pct. Zn	EMF of Cell, mV
28	94.43	487.7
29	89.82	484.5
30	84.46	481.0
31	80.32	477.4
32	76.96	473.4
33	73.17	469.1
34	69.56	464.5

B. A copper-zinc alloy containing from about 5.5% to about 13.0% of zinc was held at 1,069° C. The EMF readings, in millivolts, across the electrochemical cell are tabulated below.

Alloy No.	Wt. Pct. Zn	EMF of Cell, mV
35	5.52	165.5
36	6.84	182.3
37	7.78	199.0
38	8.97	213.7
39	10.30	229.2
40	11.26	242.5
41	12.08	250.6
42	12.92	256.4

The nickel concentration in a copper-nickel alloy melt may be measured using a nickel/nickel oxide reference electrode in a zirconium oxide-calcium oxide electrolyte. Where the system has a low chemical potential it is preferable to use an electrolyte of doped thorium oxide.

Where a system using a particular reference electrode develops large electromotive forces thus giving rise to possible electrode polarization it is preferable to use a reference electrode other than nickel/nickel oxide. Thus in measuring the aluminum concentration in aluminum-bronze melts it is preferred to use a chromium/chromic oxide reference electrode in a thorium oxide electrolyte doped with calcium oxide or magnesium oxide. Chromium concentration in stainless steel melts is measured using the chromium/chromic oxide reference electrode.

In one embodiment of this invention it is contemplated that the electrochemical or galvanic cell may be adapted to be inserted directly into the melting vessel containing the molten metal.

In another embodiment within the scope of this invention the galvanic cell is suspended in a vessel such as an alumina crucible. The crucible and cell are placed in a small furnace conveniently located near the melting pot. The furnace is maintained at a temperature complimenting that of the molten metal alloy in the melting pot. In operation, a molten metal sample is removed in any convenient manner from the melting pot and transferred immediately to the crucible in the furnace. The EMF of the galvanic cell is then measured on a potentiometer to determine the concentration of a metal in the molten metal.

What I claim is:

1. A method of determining the concentration of zinc in molten brass containing at least 0.005 parts per million oxygen which comprises:

a. preparing a bath of molten brass,

b. taking samples of said molten brass at time intervals while adding zinc to said molten brass,

c. measuring the electromotive force across a galvanic cell inserted into said molten brass simultaneously with the taking of each sample, wherein one electrode comprises said molten brass, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as said molten brass and the electrolyte is a solid anionic conductor,

d. analyzing each sample for zinc,

e. plotting calibration curves of zinc versus electromotive force based on electromotive force measurements from step (c) and zinc analyses from step (d), and

f. in a second bath of molten brass containing at least 0.005 parts per million oxygen, measuring in said second bath the electromotive force as in step (c) and obtaining from the calibration curve plotted in step (e) the concentration of zinc in said second bath of molten brass.

2. A method of determining the concentration of nickel in molten copper-nickel alloys containing at least 200 parts per million oxygen which comprises:

a. preparing a bath of molten copper-nickel alloy,

b. taking samples of said molten copper-nickel alloy at time intervals while adding nickel to said molten copper-nickel alloy,

c. measuring the electromotive force across a galvanic cell inserted into said molten copper-nickel alloy simultaneously with the taking of each sample, wherein one electrode comprises said molten copper-nickel alloy, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as said molten copper-nickel alloy and the electrolyte is a solid anionic conductor,

d. analyzing each sample for nickel,

e. plotting calibration curves of nickel versus electromotive force based on electromotive force measurements from step (c) and nickel analyses from step (d), and

f. in a second bath of molten copper-nickel alloy containing at least 200 parts per million oxygen, measuring in said second bath the electromotive force as in step (c) and obtaining from the calibration curve plotted in step (e) the concentration of nickel in said second bath of molten copper-nickel alloy.

3. A method of determining the concentration of aluminum in molten aluminum-bronzes containing at least 1.0 parts per million oxygen which comprises:

a. preparing a bath of molten aluminum-bronze,

b. taking samples of said molten aluminum-bronze at time intervals while adding aluminum to said molten aluminum bronze alloy,

c. measuring the electromotive force across a galvanic cell inserted into said molten aluminum-bronze simultaneously with the taking of each sample, wherein one electrode comprises said molten aluminum-bronze, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as said molten aluminum-bronze and the electrolyte is a solid anionic conductor,

d. analyzing each sample for aluminum,

e. plotting calibration curves of aluminum versus electromotive force based on electromotive force measurements from step (c) and aluminum analyses from step (d), and

f. in a second bath of molten aluminum-bronze containing at least 1.0 parts per million oxygen, measuring in said second bath the electromotive force as in step (c) and obtaining from the calibration curve plotted in step (e) the concentration of aluminum in said second bath of molten aluminum-bronze.

4. A method of determining the concentration of chromium in molten stainless steel containing at least 1.0 parts per million oxygen which comprises:

a. preparing a bath of molten stainless steel,

b. taking samples of said molten stainless steel at time intervals while adding chromium to said molten stainless steel,

c. measuring the electromotive force across a galvanic cell inserted into said molten stainless steel simultaneously with the taking of each sample, wherein one electrode comprises said molten stainless steel, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as said molten stainless steel and the electrolyte is a solid anionic conductor,

d. analyzing each sample for chromium,

e. plotting calibration curves of chromium versus electromotive force based on electromotive force measurements from step (c) and chromium analyses from step (d), and

f. in a second bath of molten stainless steel containing at least 1.0 parts per million oxygen, measuring in said second bath the electromotive force as step (c) and obtaining from the calibration curve plotted in step (e) the concentration of chromium in said second bath of molten stainless steel.

5. A method of measuring the concentration of a metal in a melt of an alloy, said metal having an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal of a molten alloy, said molten alloy selected from the group consisting of copper-nickel alloys, aluminum-bronzes, brasses and stainless steels, wherein said metal having an oxide which has an oxygen potential less than that of the oxygen normally dissolved in the solvent metal is nickel in molten copper-nickel alloys, aluminum in molten aluminum-bronzes, zinc in molten brasses, and chromium in molten stainless steels, which method comprises:

a. preparing a bath of a molten alloy selected from the group consisting of copper-nickel alloys containing at least 200 parts per million oxygen, aluminum-bronzes containing at least 1 part per million oxygen, brasses containing at least 0.005 parts per million oxygen, and stainless steels containing at least 1 part per million oxygen,

b. taking samples of said molten alloy at time intervals while adding nickel to said copper-nickel alloys, aluminum to said aluminum-bronzes, zinc to said brasses and chromium to said stainless steels,

c. measuring the electromotive force across a galvanic cell inserted into said molten alloy simultaneously with the taking of each sample, wherein one electrode comprises said molten alloy, the other electrode is a reference electrode comprising a mixture of a metal and its oxide or a gas of known oxygen potential at the same temperature as said molten alloy and the electrolyte is a solid anionic conductor,

d. analyzing each sample for nickel in said copper-nickel alloys, aluminum in said aluminum-bronzes, zinc in said brasses and chromium in said stainless steels,

e. plotting calibration curves of nickel versus electromotive force, aluminum versus electromotive force, zinc versus electromotive force, and chromium versus electromotive force based on electromotive force measurements from step (c) and nickel, aluminum, zinc and chromium analyses from step (d), and

f. in a second bath of a molten alloy selected from the group consisting of copper-nickel alloys containing at least 200 parts per million oxygen, aluminum-bronzes containing at least 1 part per million oxygen, brasses containing at least 0.005 parts per million oxygen and stainless steels containing at least 1 part per million oxygen, measuring in said second bath the electromotive force as in step (c) and obtain from the appropriate calibration curve plotted in step (e) the concentration of nickel in said second bath of molten copper-nickel alloy, aluminum in said second bath of molten aluminum-bronze, zinc in said second bath of molten brass and chromium in said second bath of molten stainless steel.

* * * * *