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Miller et al.

[11] **3,820,380**

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[54] **SAMPLING MOLTEN METAL BATHS**

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[52] **U.S. Cl.** ..... **73/19,** 23/230 PC, 23/230 C, 23/253 PC, 23/254 R, 73/23.1, 73/425.4 R, 73/DIG. 9

[51] **Int. Cl.** **G01n 1/10,** G01n 31/08

[58] **Field of Search**... 73/19, 23.1, 425.4 R, DIG. 9; 23/230 PC, 253 PC, 232 C, 254 R, 254 E; 75/60, 57

[56] **References Cited**

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[57] **ABSTRACT**

The concentration of a constituent in a molten bath is quickly determined by obtaining a sample in a reactor to form gaseous product related to the constituent, removing the gaseous product to an analytical zone and analyzing. For example, in determining the active oxygen content of a molten steel bath, a sample is obtained in a chamber where it contacts carbon whereby active oxygen is converted to carbon monoxide which is swept in a stream of carrier gas to a gas chromatographic station.

25 Claims, 5 Drawing Figures

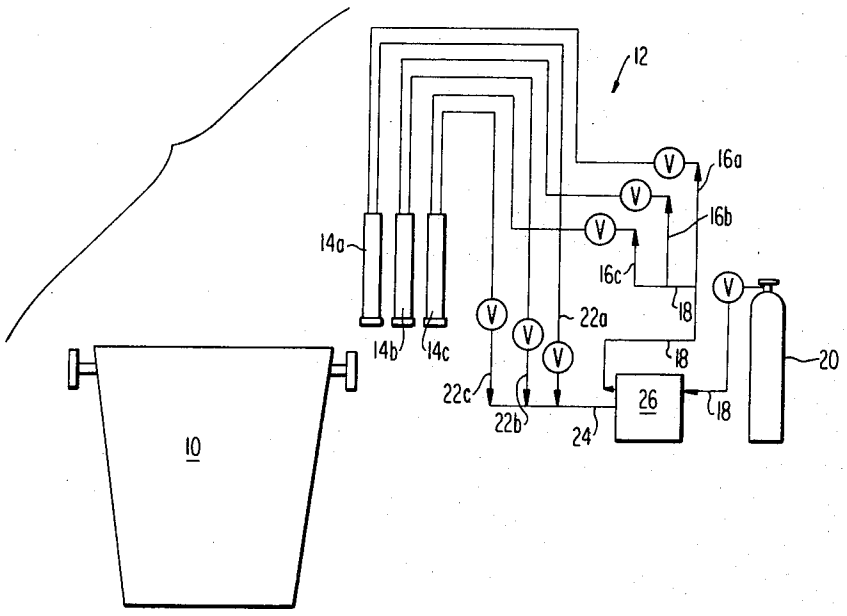


FIG. 1

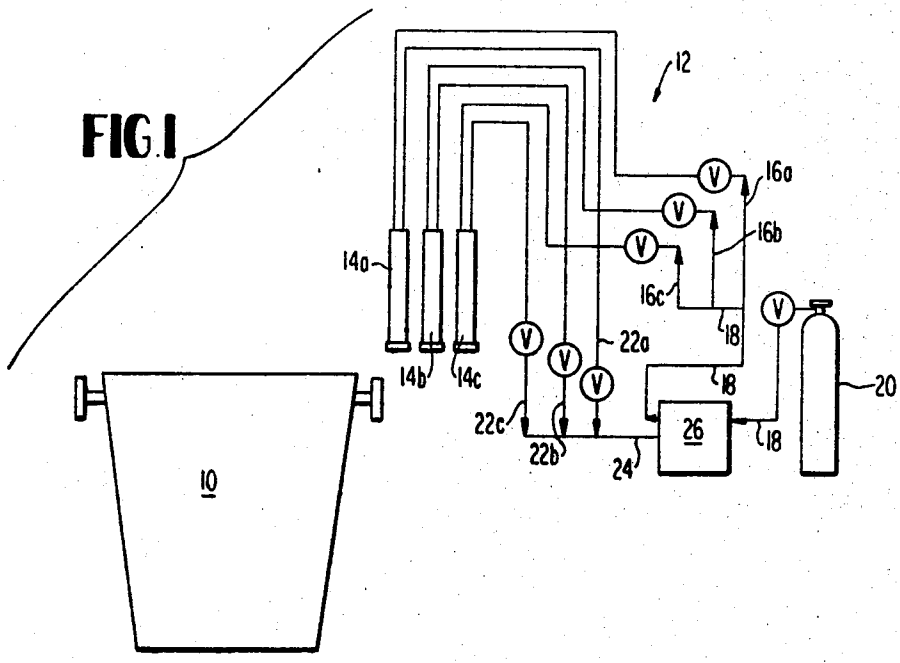


FIG. 2

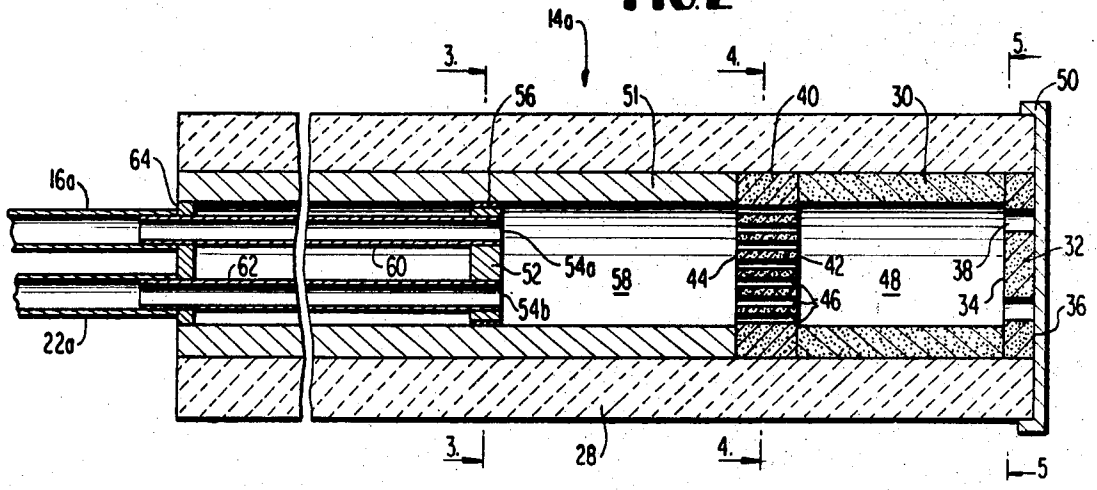


FIG. 3

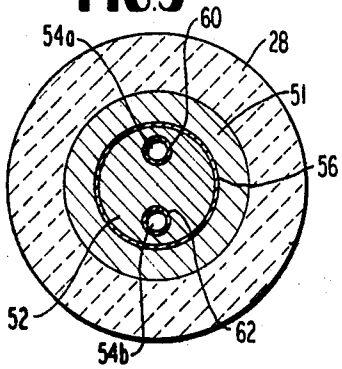


FIG. 4

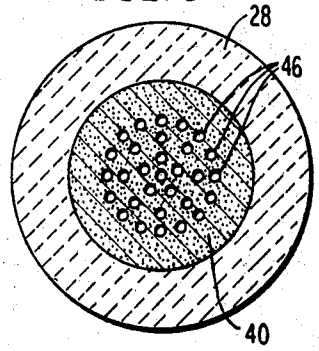
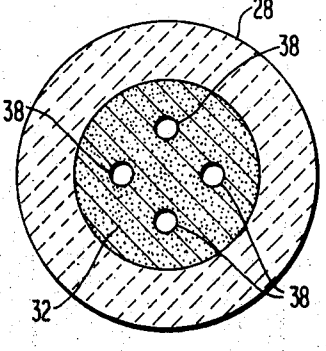


FIG. 5



SAMPLING MOLTEN METAL BATHS

BACKGROUND OF THE INVENTION

This invention relates to system and method for determining the concentration of a constituent in a molten metal bath and also to a preferred sampler-reactor for the system.

The invention is particularly useful in determining oxygen content of a molten steel bath, for example during vacuum degassing to ascertain the amount of aluminum to be added or late in a blow in the basic oxygen furnace (BOF) to determine recovery on alloy additions. It is also useful late in the blow in the BOF to determine carbon levels to arrive at precise turndown times.

U.S. Pat. No. 2,336,075 discloses two ways of analyzing for oxygen in molten steel. Firstly, the patent discloses a "bomb method" in which aluminum is placed in a cast iron bomb provided with a thin metal cover and the bomb is placed in a steel bath; the thin metal cover melts, the steel flows into the bomb and the iron oxide in the steel converts the aluminum to alumina; the bomb is removed from the bath and the contents analyzed for slumina either by a turbidity method involving treatment with acid and measuring the turbidity of the solution or by a vacuum fusion treatment to reduce the alumina. Secondly, the patent discloses a method comprising obtaining a sample in a spoon and freezing it as rapidly as possible by pouring it into a copper mold, breaking off a portion of from 10 to 20 grams, introducing this portion into a graphite crucible, then heating under vacuum whereby carbon dissolved in the steel reacts with oxygen in the steel to form carbon monoxide and collecting evolved gases in a known volume reservoir and measuring the pressure. Each of these methods is relatively time-consuming and complicated.

In a method different from the above which is being utilized, a Haly dipper is used to take a cylindrical sample (about 1 inch in diameter and about 3 inches long) which after solidification is transferred to a laboratory where it is allowed to cool further, cut to a particular size, polished to remove surface oxidation present due to exposure of the sample during transfer to the laboratory, punched, remelted in a graphite crucible whereby the carbon of the crucible reacts with oxygen in the sample to form carbon monoxide and the carbon monoxide is swept to a gas chromatograph using helium as a carrier gas. This method requires about 10 minutes.

It is an object of the present invention to provide a method and system which is significantly more rapid than the above in that it provides results in 2 to 3 minutes or less. In determining the oxygen content of a bath of molten steel, such rapid results offer maximum aid to the operators and enable more precise control for example of oxygen removal and alloy additions.

This object and others will be evident from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a schematic diagram showing a vessel for containing molten metal and a preferred system in accordance with the invention for rapidly determining oxygen content of the metal.

FIG. **2** is a sectional view of a preferred sampler-reactor for a system in accordance with the invention.

FIG. **3** is a sectional view taken at line **3—3** of FIG. **2.**

FIG. **4** is a sectional view taken at line **4—4** of FIG. **2.**

FIG. **5** is a sectional view taken at line **5—5** of FIG. **2.**

DETAILED DESCRIPTION

Referring to FIG. **1,** reference numeral **10** denotes a vessel for containing molten steel which is hereinafter referred to as a ladle, and reference numeral **12** denotes a system in accord with the present invention useful for determining, for example, the oxygen content of a molten steel bath in the ladle **10.** The system **12** includes three sampler-reactors denoted **14***a*, **14***b* and **14***c* respectively. Conduit means **16***a* contains a valve and communicates at its downstream end with an inlet into sampler-reactor **14***a*. Conduit means **16***b* contains a valve and communicates at its downstream end with an inlet into sampler-reactor **14***b*. Conduit means **16***c* contains a valve and communicates at its downstream end with an inlet into sampler-reactor **14***c*. The conduit means **16***a*, **16***b* and **16***c* each communicate at their upstream ends with a header **18.** The header **18** contains a valve and communicates at its upstream end with a source of gas depicted as pressurized tank **20.** A conduit **22***a* contains a valve and communicates at its upstream end with an outlet from sampler-reactor **14***a*. A conduit **22***b* contains a valve and communicates at its upstream end with an outlet from sampler-reactor **14***b*. A conduit **22***c* contains a valve and communicates at its upstream end with an outlet from sampler-reactor **14***c*. The conduits **22***a*, **22***b* and **22***c* each communicate at their downstream ends with a header **24** which in turn communicates with a gas chromatograph **26.** The chromatograph **26** is also in communication with header **18** at a location between the valve in header **18** and where header **18** is in communication with conduit means **16***a*, **16***b* and **16***c*. The conduits **16***a*, **16***b*, **16***c*, **22***a*, **22***b* and **22***c* are of flexible material so as to be easily extended and retracted during use. Preferably, the chromatograph is positioned 15 to 30 feet from ladle **10** so as to be protected from the hostile environment associated with the ladle.

Referring to FIG. **2,** a sampler-reactor denoted **14***a* (**14***b* and **14***c* are structurally the same) has an elongated cylindrical exterior configuration.

The cylinder sidewall is defined by tubular member **28.** Member **28** is composed of refractory material such as ceramic material so as to protect the sampler-reactor when it is inserted into molten metal as described later.

Toward the forward end of the sampler-reactor is an annular tube **30.** The tube **30** has an outer diameter equal to the inner diameter of tube **28** and is coaxial therewith. Tube **30** is composed of graphite.

Forward of tube **30** is a disc-shaped element **32.** The element **32** is coaxial with tube **28** and has a diameter equal to the inner diameter of tube **28.** The element **32** has an inner face **34** which toward its periphery butts up against the forward end of tube **30.** It has an outer face **36** which is coplanar with the forward end of tube **28.** The element **32** is composed of graphite. With reference to FIG. **5,** the element **32** contains four holes **38**

each extending axially therethrough. The holes are spaced inwardly from the sidewall of element **32** so as to provide communication into the interior of tube **30.**

A disc-shaped element **40** is directly rearward of tube **30.** Element **40** has a diameter equal to that of the inner diameter of tube **28** and is coaxial therewith. It has a forward surface **42** which toward its periphery butts up against the rearward end of tube **30.** It has a rearward surface **44.** The element **40** is composed of graphite. With reference to FIG. **4,** element **40** contains a multiplicity of axially extending passageways **46,** for example **20** to **40** of such passageways. These passageways each have a diameter sufficiently large so that gas can pass therethrough but sufficiently small so that molten metal will not pass therethrough. Preferably these passageways have diameters ranging from about 0.020 to about 0.040 of an inch.

The elements **30, 32** and **40** coact to provide a sample-receiving chamber **48.** The chamber **48** is of substantially cylindrical configuration. It is coaxial with tube **28.** It has a sidewall provided by the inner surface of element **30,** a forward endwall provided by a portion of the inner face **34** of member **32** and a rear endwall provided by a portion of the forward surface **42** of element **40.** Inlets into chamber **48** are provided by holes **38** and outlet means from chamber **48** is provided by passageways **46.**

A cap **50** is at the forward end of the sampler-reactor. It is fitted over the forward end of tube **28.** It protects element **32** from exposure to the environment and prevents foreign material from entering through passageways **38** into chamber **48** thereby isolating chamber **48** from the atmosphere and contaminants. The cap **50** is of a thickness and composed of metal such as to melt when inserted into a molten metal bath thereby exposing holes **38** to the molten bath so that molten metal can enter chamber **48** therethrough.

A tube **51** extends starting just back of element **40.** It is coaxial with tube **28** and has an outer diameter equal to the inner diameter of tube **28.** It has an inner diameter the same as the inner diameter of tube **30.** It has a forward end which butts up against surface **44** of element **40.** It has a rearward end which is coplanar with the rearward end of tube **28.** It is composed of steel.

Within tube **51** spaced from element **40** is a disc-shaped element **52.** The element **52** is coaxial with tube **28.** It is composed of steel. With reference to FIG. **3,** the element **52** contains two passageways extending axially therethrough, an inlet passageway **54***a* and an outlet passageway **54***b*. The passageways **54***a* and **54***b* are positioned symmetrically with respect to element **52.**

O-ring **56** provides fluid-tight sealing engagement between element **52** and the interior wall of tube **51.**

A chamber **58** for receiving gaseous product from chamber **48** through passageways **46** is defined by a portion of rear surface **44** of element **40,** a portion of the interior sidewall surface of element **51** and the forward face of element **52.**

Fastened into the passageway **54***a* is the downstream end of a tube **60.** This tube is positioned axially within tube **28** and extends slightly beyond the plane of the rearward ends of tube **28** and tube **51.** Tube **60** is composed of steel. As previously indicated a different conduit means communicates with an inlet of each sampler-reactor and the particular conduit means communicating with sampler-reactor **14***a* is denoted **16***a*. The conduit means **16***a* is in the form of a carrier gas inlet pipe and such connects with the portion of tube **60** extending beyond the plane of the end of tube **28** whereby carrier gas may be fed into tube **60.** Conduits **16***b* and **16***c* are connected in similar fashion respectively with sampler-reactors **14***b* and **14***c*.

A tube **62** is fastened at its upstream end into the other passageway **54***b* and extends rearwardly therefrom axially in relation to tube **28.** It extends slightly past the plane of the rearward end of tube **28.** It is composed of steel. As previously indicated a different conduit communicates with the outlet of each sampler-reactor and the particular conduit communicating with the outlet of sampler-reactor **14***a* is denoted **22***a*. The conduit **22***a* is in the form of a gas outlet tube which is fastened to the end of tube **62** extending beyond the plane of the face of the rearward end of tube **28** so that gas may pass from tube **62** into tube **22***a*. Conduits **22***b* and **22***c* are connected in similar fashion respectively with sampler-reactors **14***b* and **14***c*. The conduits **22***a*, **22***b* and **22***c* respectively provide in combination with header **24** direct communication between sampler-reactors **14***a*, **14***b* and **14***c* and chromatograph **26.**

A disc-shaped element **64** is positioned within element **51** at its rearward end so as to have its rear face coplanar with the rear faces of elements **28** and **51.** It has passageways therein corresponding to the passageways **54***a* and **54***b* of element **52** and tubes **60** and **62** extend through these passageways whereby member **64** supports tubes **60** and **62** axially of element **28.**

The operation of the above system is now described for purposes of convenience where ladle **10** is a degassing vessel and the temperature of the molten steel is in the range of temperatures normally encountered during degassing. The system is used to measure the concentration of active oxygen in the molten steel. The term "active oxygen" is used to include both free and combined oxygen except that combined with aluminum and that combined with silicon under the degassing conditions.

While three sampler-reactors have been depicted in FIG. **1,** only one is used at a time. The operation is therefore described in detail with respect to a single sampler-reactor **14***a*. The operation of sampler-reactors **14***b* and **14***c* is described thereafter.

When sampler-reactor **14***a* is utilized the valve in conduit **18** is maintained open as well as the valves in conduits **16***a* and **22***a* while the valves in conduits **16***b*, **16***c*, **22***b* and **22***c* are maintained closed.

In operation, the sampler-reactor **14***a* is introduced into a bath of molten steel in ladle **10.** When the forward end of the sampler-reactor enters the bath, cap **50** melts off and molten steel flows through passageways **38** into chamber **48** substantially filling that chamber. A molten sample is thereby obtained in chamber **48.** The amount of the sample is predetermined by the volume of chamber **48.**

As the molten steel enters chamber **48,** the graphite wall structure of elements **30, 32** and **40** provides a source of carbon, that is a carbonaceous environment, so that the carbon level in the sample builds up to, for example 0.5 percent so that the equilibrium level of active oxygen therein is very low, e.g. less than 15 p.p.m. The active oxygen in excess of this equilibrium level reacts with carbon in the carbonaceous environment to form carbon monoxide prior to the freezing of the steel.

Thus chamber **48** functions as a zone for obtaining and isolating a molten sample; as a zone where reactant and in particular carbon in the carbonaceous environment provided by the wall structure of the chamber builds up in the molten sample to lower the equilibrium level of active oxygen in the sample to a point where said equilibrium level is low enough so that it can be ignored or readily corrected for; and as a reaction zone where the sample still in molten state and in particular the active oxygen in the sample in excess of the newly provided lower equilibrium level is reacted to form the gaseous product carbon monoxide which is stoichiometrically related to the active oxygen constituent being analyzed for.

Carrier gas, preferably helium or argon, from pressurized cylinder **20** passes through header **18** into inlet conduit **16***a*, then into tube **60** and then through passageway **54***a* into the chamber **58.**

The carbon monoxide as it is formed flows from chamber **48** through passageways **46** of element **40** into chamber **58.** The carrier gas entering chamber **58** provides a driving force for removing the carbon monoxide directly, that is without delay, to chromatograph **26.** In particular, the carbon monoxide is swept from that chamber and thereby sweeps the carbon monoxide from chamber **58** through tube **62** into outlet conduit **22**a.

The gas in conduit **22***a* passes to header **24** and into the analytical zone defined by chromatograph **26** whereby a reading on the level of carbon monoxide is provided. The communication of header **18** with the chromatograph **26** provides a reference whereby any effect of the composition of the carrier gas on the reading obtained is eliminated. The reading obtained is in the form of a peak on a graph. This data is translated into concentration of oxygen by comparison to standard graphs. The standard graphs are obtained for a particular system by utilizing the system to obtain a graph and simultaneously obtaining a different sample which is conventionally analyzed; by doing this a number of times a set of graphs are obtained with each particular graph corresponding to a particular concentration.

In the above, the chamber **58** functions as a removal zone, that is as a zone whereby the formed gaseous product is removed to an analytical zone, namely the chromatograph.

The construction of sampler-reactor **14***a* is such that the molten metal entering chamber **48** is allowed to remain molten for sufficient time (20 to 40 seconds) that substantially all of the active oxygen in the sample is driven out therefrom and converted into carbon monoxide and so that at the time when or soon after this has occurred the sample solidifies so as to seal the forward end of chamber **48** so that extraneous constituents do not interfere with the accuracy of the analytical results.

It is important that the carrier gas be quantitatively analytically distinct from the carbon monoxide under the analytical conditions utilized. In view of the fact that gas chromatographic analysis is utilized, this is accomplished by selecting a carrier gas having a molecular weight substantially different from that of the carbon monoxide. The carrier gas should also be one which does not adversely affect the carbon monoxide. Carrier gases preferred for use in the above particularly described embodiment are selected from the group consisting of helium and argon.

Utilizing the above procedure a reading on the gas chromatograph is typically obtained in two to three minutes or less after sampling is initiated. This time period is significantly more rapid than analytical time periods accomplished previously and allows operators to make for example on the spot adjustments, for example adjustments in aluminum addition during degassing. Furthermore, it has the advantage when the above is utilized in determining the oxygen content late in the blow in the BOF of providing data whereby alloy recoveries can be accurately determined; in other words, whereby it can be determined rapidly how much of an alloying agent should be added to obtain a particular level in the final product.

With the apparatus depicted in FIG. **1** a second analysis is ready to be obtained on completion of the first analysis by simply closing valves **16***a* and **22***a* and opening valves **16***b* and **22***b* and inserting sampler-reactor **14***b* into the molten metal.

With corresponding manipulation of the valves, a third analysis can be taken utilizing sampler-reactor **14***c*.

Thus, with the depicted embodiment (FIG. **1**) three successive analyses can be taken. Inasmuch each analysis takes three minutes or less, the three successive analyses can be obtained in less than ten minutes which is the time period which has heretofore been necessary in practice to obtain a single analytical result.

A detailed description of the most preferred embodiment of sampler-reactor follows. The sampler-reactor is that depicted in FIG. **2.** The elements **30, 32** and **40** are of spectrographically pure graphite. The diameter of chamber **48** is ½ inch. The length of chamber **48** is ¾inch. The wall thickness of element **30** is ⅛ inch. The axial dimension of element **32** is ⅛ inch. Each of the holes **38** in element **32** has a diameter of 3/32 of an inch. The axial dimension of member **40** is ¼ inch. Member **40** contains **30** closely spaced passageways each 0.030 of an inch in diameter. Chamber **58** has an axial dimension of **1** inch and a diameter of ½ inch. Element **51** has a thickness of ⅛ inch and an axial dimension of 4 feet. It is made of steel. Each of the passageways **54***a* and **54***b* of element **52** has a diameter of ⅛ inch. Element **52** is made of steel. O-ring **56** is made of Viton. Each of the tubes **60** and **62** are steel pipes having outside diameters of ⅛ inch. Element **64** is made of steel. Element **28** is ¼ inch thick and made of ceramic material. Cap **50** is made of **18** gage steel. The sampler-reactor so constructed is utilized to determine the active oxygen content in a ladle of molten steel during degassing. The temperature of the molten steel is about 2,900° F. The forward end of the sampler-reactor is inserted into the steel bath. When the sampler-reactor is inserted, cap 50 melts off and molten steel enters substantially filling chamber **48.** The weight of the sample obtained is approximately 40 grams. The molten steel enters the chamber **48** through the passageways **38.** As it so enters and contacts the carbonaceous environment in the form of the graphite members **30, 32** and **40,** the carbon level in the sample builds up to the point where it contains about 0.5 percent carbon and the equilibrium level of active oxygen in the sample is about 5 p.p.m. by weight. The oxygen driven out from the sample due to the equilibrium shift reacts with the carbonaceous environment in the form of the walls **30,**

32 and **40** and is converted to carbon monoxide which is passed through passageways **46** into chamber **58.** The sample remains molten for about 30 seconds after the sampler is inserted into the bath, whereupon the sample solidifies to the extent that passageways **38** are blocked. A stream of helium gas is passed from tank **20** through header **18** and conduit **16***a* into the sampler-reactor and passes through tube **60,** passageway **54***a* and element **52** into chamber **58** wherein it picks up the carbon monoxide in chamber **58** and sweeps it out of chamber **58** through tube **62.** The gas leaving chamber **58** after passing through tube **62** passes into tube **22***a* and then into header **24** and then is directed to the gas chromatograph **26.** The distance of the chromatograph from the ladle is about 15 feet, and this is a distance sufficiently far as to provide security from the hostile environment of the ladle. The gas chromatograph provides a peak reading which is translated by reference to standard graphs as previously described into active oxygen content, for example 150 p.p.m. active oxygen indicating to the operator the extent of degassing. The analytical result is obtained in less than 2 minutes.

All percentages and parts herein are by weight unless otherwise stated.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof.

For example, the above system can be utilized to obtain a reading on the level of carbon in a molten steel bath. This can be done because active oxygen and carbon are in equilibrium in a molten steel bath. Thus, with equilibrium data at the particular temperature concerned, the reading on the gas chromatograph can be converted into a determination of carbon content. This analysis for carbon level is useful late in the blow in the BOF to arrive at precise turndown times.

Furthermore, the system can be utilized to determine the concentration of constituents in molten metal baths other than molten steel baths, for example the system is useful in determining the oxygen content in a bath of molten copper. Such reading is important because the oxygen content in copper is controlled to adjust workability. Oxygen is added by poling, i.e., by inserting green poles into a molten copper bath. The use of the above described system is helpful in determining the amount of poling to obtain a given degree of workability.

Moreover, different sample-receiving chambers from the one specifically described before can be utilized so long as the chamber contains a suitable inlet and outlet and so long as a very large excess of reactant is provided. The element **40** can, for example, be porous instead of containing a definite number of distinct passageways; where the reactant is carbon, element **40** can be composed of porous graphite. The excess of reactant can be for example on the order of 100 times stoichiometric or more.

Moreover, a control integrator can be utilized to electronically convert the chromatographic output to a numerical readout or the output from the chromatograph might be fed to a computer input.

Moreover, other types of gas analyzers may be utilized instead of gas chromatographs as long as they can quantitatively analyze for the gaseous product; for example an infrared analyzer can be utilized.

Moreover, a system can be provided with only a single sampler-reactor or any number of sampler-reactors.

Furthermore, the sampler-reactor can carry a temperature sensing device so that a temperature reading is obtained at the same time a concentration determination is obtained.

In view of the variations that are readily understood to come within the limits of the invention, such limits are defined by the scope of the appended claims.

What is claimed is:

1. Method of determining the concentration of a constituent in a molten metal bath comprising the steps of

obtaining a molten sample from the bath in a reaction zone,

reacting said sample still in molten state in said zone to form gaseous product related to said constituent,

removing said product directly to an analytical zone,

and quantitatively analyzing for said product.

2. Method as recited in claim **1** for determining the concentration of active oxygen in a bath of molten steel.

3. Method as recited in claim **2** wherein the reaction zone comprises a carbonaceous environment whereby the carbon level in the molten sample builds up to the point where the equilibrium level of active oxygen in the sample is less than 15 p.p.m.

4. Method as recited in claim **3** wherein said step of reacting said sample comprises reacting the active oxygen in excess of said equilibrium level with carbon in said carbonaceous environment and the gaseous product formed is carbon monoxide.

5. Method as recited in claim **4** comprising allowing said sample to remain molten for 20 to 40 seconds.

6. Method as recited in claim **4** wherein the step of removing the gaseous product to an analytical zone comprises passing gaseous product to a removal zone, introducing a stream of carrier gas analytically distinct from the product gas into the removal zone and removing a stream of gas containing product gas from the removal zone utilizing the carrier gas stream as the driving force.

7. Method as recited in claim **6** wherein the step of analyzing comprises gas chromatographic analysis.

8. Method as recited in claim **7** wherein the carrier gas has a molecular weight substantially different from that of the gaseous product.

9. Method as recited in claim **8** wherein the carrier gas is selected from the group consisting of helium and argon.

10. System for determining the concentration of a constituent in a molten metal bath comprising

a. sampler-reactor including

i. means to isolate a sample of molten metal from said bath,

ii. a source of reagent in means (i) which reacts to form gaseous product related to said constituent,

iii. means to remove gaseous product including carrier gas inlet means and gas outlet means;

b. first conduit means communicating with said inlet means;

c. a source of carrier gas communicating with said first conduit means; and

d. means directly communicating with said gas outlet means for quantitatively analyzing gaseous product.

11. System as recited in claim **10** wherein the source of reagent is a source of carbon.

12. System as recited in claim **11** wherein the carbon is in the form of spectrographically pure graphite.

13. System as recited in claim **10** wherein the source of carrier gas is a source of helium.

14. System as recited in claim **10** wherein said means (e) is a gas chromatograph.

15. Sampler-reactor comprising

a. means defining a chamber for receiving a sample from a bath of molten metal comprising wall means composed of a source of reagent which reacts with a constituent of the sample to form gaseous product, said chamber means having a forward end and a rearward end;

b. means defining said forward end including molten metal inlet means;

c. means defining said rearward end including outlet means for gaseous product;

d. means defining a chamber for receiving gaseous product from the outlet means of element (c) and including gaseous product inlet means, carrier gas inlet means and gas outlet means.

16. Sampler-reactor as recited in claim **15** wherein the rearward end of the sampler-receiving chamber is a wall common to the gaseous product-receiving chamber.

17. Sampler-reactor as recited in claim **16** wherein said wall contains a multiplicity of orificies providing the outlet means of element (c) and communication between the sample-receiving chamber and the gaseous product-receiving chamber.

18. Sampler-reactor as recited in claim **17** wherein the forward end of the sample-receiving chamber is a wall containing orifice means providing the molten metal inlet means of element (b).

19. Sampler-reactor as recited in claim **18** wherein the wall at the forward end of the sample-receiving chamber has its exterior protected by a cap which melts off when inserted into a molten metal bath.

20. Sampler-reactor as recited in claim **18** wherein the sample-receiving chamber is substantially cylindrical comprising sidewall in addition to the walls at the forward and rearward ends and said sidewall and forward and rearward walls are composed of carbon.

21. Sampler-reactor as recited in claim **20** wherein the carbon is in the form of spectrographically pure graphite.

22. Sampler-reactor as recited in claim **18** wherein the gaseous product-receiving chamber is substantially cylindrical having a wall at its rearward end containing orifice means providing the carrier gas inlet means of element (d) and other orifice means providing the gas outlet means of element (d).

23. Sampler-reactor as recited in claim **15** additionally comprising a first conduit means communicating with the carrier gas inlet means of element (d) and a second conduit means communicating with the gas outlet means of element (d)

24. Sampler-reactor as recited in claim **15** having an elongated cylindrical exterior configuration with the cylinder sidewall comprising refractory material and a forward end protected by a melt-off cap.

25. System for determining the concentration of a constituent in a molten metal bath comprising

a. sampler-reactor including

i. means defining a chamber for receiving a sample from a bath of molten metal comprising wall means composed of a source of reagent which reacts with a constituent of the sample to form gaseous product, said chamber having a forward end and a rearward end;

ii. wall means defining said forward end, containing orifice means providing molten metal inlet means;

iii. wall means defining said rearward end containing means providing outlet means for gaseous product from means (i);

iv. means defining a chamber for receiving gaseous product from the outlet means of means (iii) and including gaseous product inlet means, carrier gas inlet means and gas outlet means;

b. first conduit means communicating with the carrier gas inlet means of means (iv);

c. a source of carrier gas communicating with said first conduit means;

d. second conduit means communicating with the gas outlet means of means (iv); and

e. means communicating with said second conduit means for quantitatively analyzing gaseous product.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,820,380 Dated June 28, 1974

Inventor(s) Gerald G. Miller and Rox L. Zickefoose

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At column 1, line 25, "slumina" should be changed to --alumina--.

At column 9, lines 1-3, "d. means directly communicating with said gas outlet means for quantitatively analyzing gaseous product." should be changed to --(d). means providing direct communication between said gas outlet means and means (e); (e) means for quantitatively analyzing gaseous product--.

Signed and sealed this 8th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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