# United States Patent [19]

**Boorstein et al.**

[11] **3,878,073**

[45] **Apr. 15, 1975**


[54] **OXYGEN EXCHANGE WITH LIQUID METALS**


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[51] **Int. Cl.** ..... **C23b 1/00;** C01b 13/04

[58] **Field of Search** ..... 204/140, 195 S, 129; 13/27, 27 S



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*Primary Examiner*—T. M. Tufariello

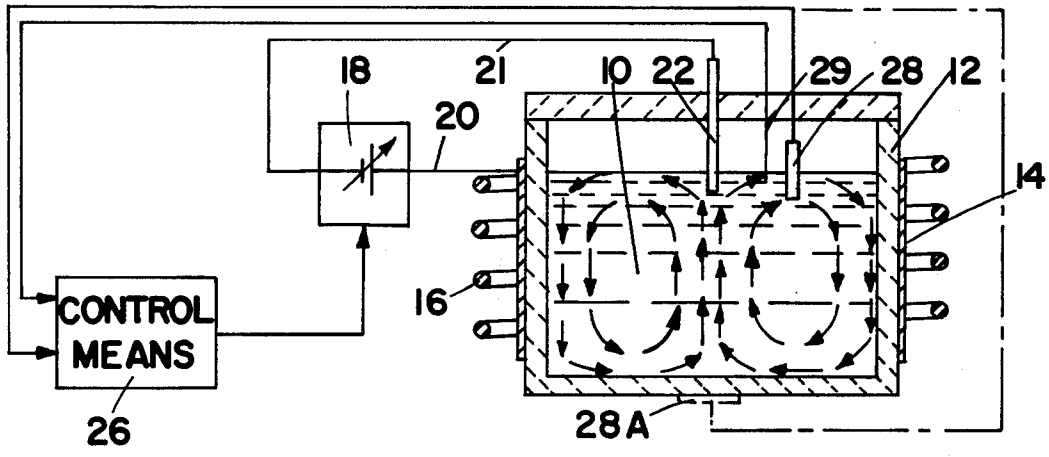
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[57] **ABSTRACT**

Oxygen, which is dissolved in liquid metals, is rapidly withdrawn by electrochemical pumping through a solid electrolyte cell while the melt is turbulently circulated past the electrolyte wall. Heating and stirring of the melt by induction or other means additionally permit a further increased deoxidation rate by allowing application of pumping voltages in excess of the electrolyte decomposition voltage for stagnant melts. A programmed reduction of pumping voltage as oxygen is withdrawn optimizes the deoxidation rate. Oxygen may similarly be pumped into the melt.


**11 Claims, 5 Drawing Figures**



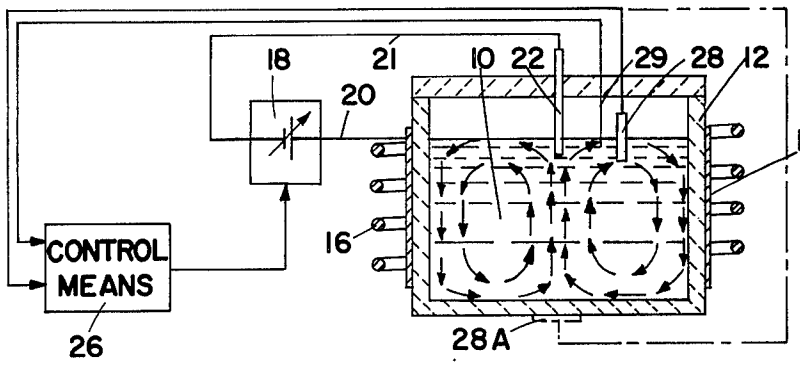



FIG. 1

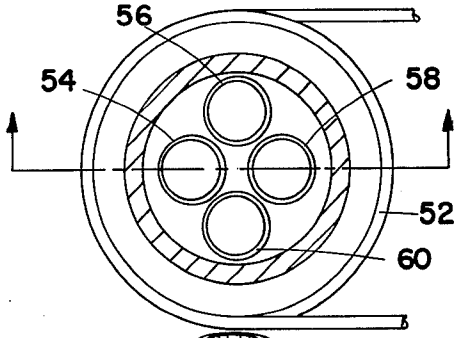



FIG. 3

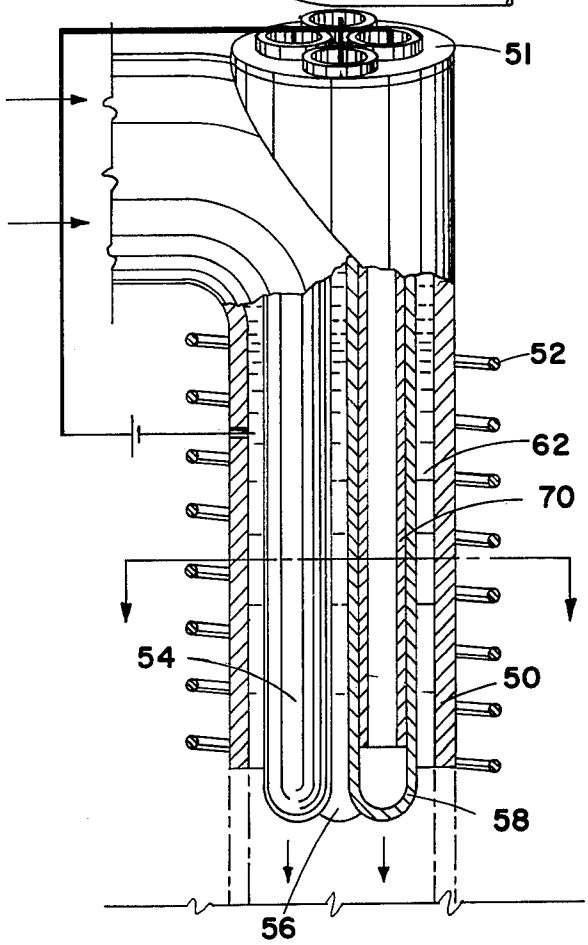
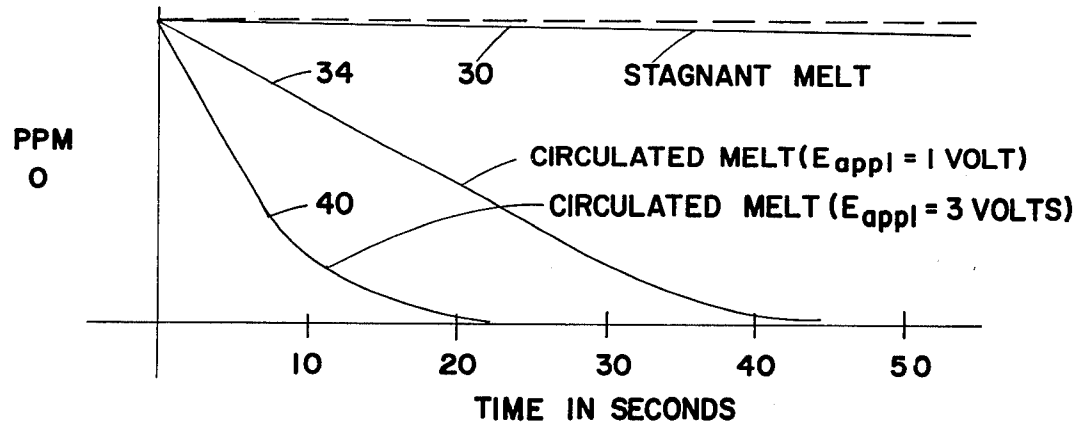



FIG. 2

FIG. 4


PPM
O
34
30
STAGNANT MELT
CIRCULATED MELT ($E_{appl}$ = 1 VOLT)
40
CIRCULATED MELT ($E_{appl}$ = 3 VOLTS)
10
20
30
40
50
TIME IN SECONDS

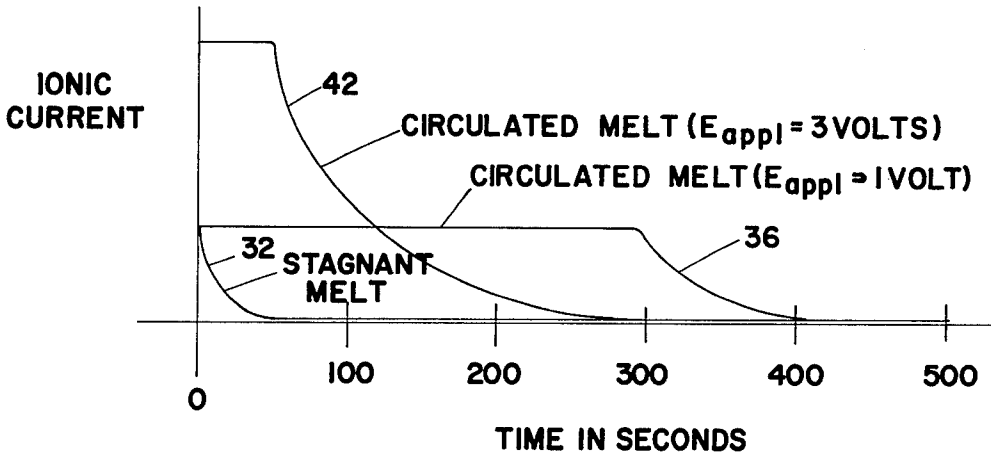

IONIC
CURRENT
42
CIRCULATED MELT ($E_{appl}$ = 3VOLTS)
CIRCULATED MELT ($E_{appl}$ = 1VOLT)
36
32
STAGNANT
MELT
0
100
200
300
400
500
TIME IN SECONDS

FIG. 5

# OXYGEN EXCHANGE WITH LIQUID METALS

## BACKGROUND OF THE INVENTION

The invention herein described was made in the course of or under a contract or subcontract thereunder, with the department of the Air Force.

This invention relates generally to the purification of metals and metallic alloys and more particularly relates to the oxidation or deoxidation of liquid metals.

One of the principal detriments to the tensile strength, fatigue behavior, and toughness of metals is the presence in their structure of impurity particles such as oxides. Oxide particles are commonly formed in alloys upon the solidification of liquid metals because the solubilities of gases in metals are significantly lower in solid metals at normal temperatures than in liquid metals.

The traditional method for the removal of oxygen from liquid metals prior to casting is by the addition of elements such as aluminum, silicon, and manganese which form very stable oxide precipitates in the liquid metal. Unfortunately however, a significant portion of the precipitates are not able to escape by flotation from the molten metal prior to solidification and are therefore trapped in the ingot or casting where they contribute to the degradation of mechanical properties.

More recently, the new methods of vacuum fusion and electroslag refining have been developed to remove gases dissolved in the liquid metal. These methods however, require expensive capital equipment and exhibit specific advantages and disadvantages for each specific alloy system with specific casting requirements.

In known metal refining processes, oxygen is often initially introduced into the melt, for example through a tube inserted in the melt, in order to remove carbon or sulfur in the form of CO and $SO_2$. After the carbon and sulphur are sufficiently removed, the melt is then deoxidized.

The solid electrolyte cell has recently been the object of experimentation in scientific studies other than refining metals. Such a cell comprises an intermediate layer, such as a tube, of solid electrolyte, such as a ceramic oxide, having electrodes deposited on or pressed against its opposite surfaces. The electrodes might be porous to permit the transport of gaseous oxygen or other oxygen containing gases into or from the solid electrolyte. Otherwise, the electrodes might be a condensed phase in which the oxygen content or activity is established.

Such solid electrolyte cells have been used both for measuring the oxygen activity of a gas and for pumping oxygen from a gas or to a gas through an electrolyte cell as is shown in the Ruka et al. U.S. Pat. No. 3,400,054.

Others have used such solid electrolyte cells for the laboratory measurement of the oxygen concentration of molten metals as shown by the Fischer and Meysson et al., U.S. Pat. Nos. 3,468,780 and 3,464,008.

We have discovered a method and apparatus for the commercially practical and feasible deoxidation or oxidation of liquid metals.

## SUMMARY OF THE INVENTION

The invention has a solid-electrolyte cell formed by a solid oxygen-ion-conducting electrolyte wall having a first surface in contact with the liquid metal and its opposite surface exposed to another oxygen transporting phase. An oxygen transmitting electrode such as porous platinum is coated on said opposite surface. The liquid metal forms the other electrode of the cell. A flow inducing means such as an induction heater circulates the liquid metal past the electrolyte. A dc power supply is connected to the cell electrodes for applying a pumping voltage to the cell, with the liquid metal normally at negative potential for deoxidation.

The method for deoxidizing liquid metal comprises the steps of inducing the liquid metal to circulate past an oxygen-ion-conducting, solid-electrolyte pumping cell and simultaneously applying a pumping voltage to the pumping cell for electrochemically pumping oxygen out of the liquid metal.

Accordingly, it is an object of the invention to provide an improved method and apparatus for the deoxidation of liquid metal.

Another object of the invention is to provide an alternative method and apparatus for introducing oxygen into liquid metal.

Another object of the invention is to increase the deoxidation rate.

Yet another object of the invention is to provide a system for the continuous deoxidation of a liquid metal for use in a continuous casting process.

Still another object of the invention is to provide a method and apparatus which permits a pumping voltage to be applied to the electrodes of the cell which far exceeds the decomposition voltage of the solid electrolyte in a stagnant system.

Another object of the invention is to improve the oxygen transport rate in the liquid metal and through the solid electrolyte.

Further objects and features of the invention will be apparent from the following specification and claims when considered in connection with the accompanying drawings illustrating the preferred embodiments of the invention.

## DESCRIPTION OF THE DRAWINGS

FIG. **1** is a diagrammatic view in side elevation illustrating a batch method and apparatus embodying the invention.

FIG. **2** is a diagrammatic view in side elevation illustrating a continuous method and apparatus embodying the invention.

FIG. **3** is a plan view of the embodiment of FIG. **2.**

FIG. **4** is a graphical illustration of the comparative improvement provided by the preferred embodiment of the invention.

FIG. **5** is a graphical illustration of the improved deoxidation rate provided by the preferred embodiment of the invention.

In describing the preferred embodiments of the invention illustrated in the drawings, specific terminology will be resorted to for the sake of clarity. However, it is not intended to be limited to the specific terms so selected and it is to be understood that each specific term includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

## DETAILED DESCRIPTION

FIG. **1** is a diagrammatic illustration of an embodiment of the invention suitable for batch processing, for example, in a laboratory or commercial plant. A liquid metal **10,** such as copper or lead, for example is con-

tained in a crucible **12** which is formed entirely of a solid electrolyte. For example, the entire wall of the crucible **12** may be formed of a ceramic oxide such as a stabilized zirconia base containing 4 to 7% by weight calcium oxide, yttrium oxide or magnesium oxide, for example.

An exterior, cylindrical, porous platinum electrode **14** is coated on the exterior wall of the electrolyte crucible **12.** The electrode **14** must be of a porous platinum or an equivalent material so as to permit the escape of oxygen which has been transported through the electrolyte to the exterior surface of the electrolyte crucible **12.** The helical coil **16** of an induction heater surrounds the cylindrical crucible **12.** Suitable fire bricks or other insulating material may be interposed between the exterior electrode **14** and the induction coil **16** to minimize the heat shock in the electrolyte during the melting of melt. Suitable space should be provided between the exterior electrode **14** and any insulation to provide an oxygen receiving fluid, such as ambient air. Preferably, ambient air is circulated through this space to carry away removed oxygen.

The liquid metal **10** contacts the interior surface of the electrolyte crucible **12** and forms the interior electrode. Therefore, an oxygen ion conducting, solid electrolyte cell is formed by the entirety of that portion of the crucible wall which is interposed between the exterior porous platinum electrode **14** and the interior liquid metal electrode **10.** A pumping voltage is applied from a DC power supply **18** to the electrodes through conductors **20, 21** and lead material. The lead is merely a suitable electronically conducting wire or material such as Chromel or an electronically conducting cermat. Preferably, the power supply **18** is variable so that a relatively large pumping voltage may be initially applied to the electrolyte cell and then be subsequently reduced as described below. A feedback control **26** may be used to provide a programmed reduction of the pumping voltage of the power supply **18.** Such a control may continuously monitor the oxygen concentration of the liquid metal **10** by means of, for example, a probe **28.** Such an oxygen concentration measuring probe is described in the patents cited above. A similar measuring cell may be constructed by fixing an electrode **28A** on the electrolyte such as the bottom of crucible **12.** A measuring cell is thereby formed by the electrode **28A,** the adjacent electrolyte and the melt. A suitable electronically conducting lead wire **29** from the melt would be used to complete the cell circuit in either case. Alternatively, the control can monitor the cell pumping current. Actual total cell current is partly electronic current and partly ionic current. The ionic current represents oxygen atoms pumped out of the melt. Therefore, ionic current integrated with respect to time represents total oxygen removed from the melt and can be used to compute the oxygen concentration remaining in the melt.

In the embodiment illustrated in FIG. **1,** operation begins with the induction of eddy currents into the metal **10** from the induction coil **16** to heat and melt the metal **10.** Depending upon the metal, the liquid metal together with the electrolyte cell is heated to a temperature in the range of approximately 800°K to 1900°K. A pumping voltage is then applied from the power supply **18** across the solid electrolyte cell formed at the walls of the crucible **12.** For deoxidation, the metal must be negative with respect to the exterior electrode. For oxidation, the polarity will be reversed. Oxygen which has been dissolved in the liquid metal begins to be transported from the interfacing boundary layer at the interface of the liquid metal and the wall of the crucible **12.**

It should also be understood that the specific geometry of FIG. **1** may be reversed in practicing the invention. A closed-end, solid electrolyte tube may be depressed into the circulated liquid metal and the outer crucible could be a conventional crucible. The oxygen would be pumped into the interior of the tube through a platinized electrode on the interior wall where it would be released. Such a tube would merely be equivalent to the electrolyte crucible wall illustrated in FIG. **1.** In fact, a similar reverse geometry is described in connection with FIG. **2.**

The oxygen is pumped from the liquid metal according to the relationship.

$$E_{appl} = i_{ion}\,\Omega_{ion} + \frac{RT}{4F}\ln\frac{P_0\ (\text{air})}{P_0\ (\text{melt})} \qquad \text{Eq. I.}$$

where $E_{appl}$ equals the voltage applied to the cell electrodes by the power supply **18**; $i_{ion}$ is the ionic current due to oxygen ions being transported through the electrolyte; $\Omega_{ion}$ is the ionic resistance of the solid electrolyte material; $R$ is the gas constant $T$ is temperature in degrees Kelvin; $F$ is Faraday's constant $P_0$ (air) is the oxygen activity of the ambient air or other gas at the exterior electrode **14**; and $P_0$ (melt) is the oxygen activity in the liquid metal at its interface with the interior electrolyte.

During pumping, the induction heater is continuously operated and serves not only to maintain the temperature of the liquid metal but further causes a stirring action or circulation illustrated in FIG. **1.**

The circulation is in the form of simultaneous small eddy currents and a bulk convection. Such circulation of the liquid metal transports dissolved oxygen to the electrolyte wal and reduces the boundary layer thickness at the wall.

This circulation of the liquid metal **10** is important because it continuously supplies liquid metal which is relatively high in dissolved oxygen from the interior of the bulk liquid metal to the vicinity of the electrolyte/-melt interface. In this manner, the oxygen concentration in the vicinity of the melt/electrolyte interface is maintained at a sufficiently high level to abundantly supply the ionic deoxidation current through the electrolyte.

We have found that this stirring minimizes the effect of the slow diffusion-limited transport of oxygen from the bulk melt which would otherwise limit the deoxidation rate as it doeos in a stagnant system.

We have found that this combination of electrochemical pumping through a solid electrolyte cell together with the circulation of the liquid metal past the electrolyte very substantially increases the deoxidation rate of the metal far above that which might be expected with uncirculated or stagnant metal and an electrolyte cell operating with ordinarily applied voltages. Additionally, it also permits the voltage applied to the cell to be very substantially increased above ordinarily applied cell voltages to even further increase the deoxidation rate.

This may be further understood by considering the fact that a solid electrolyte, which in this case is an oxide, has, for any given temperature, an associated equilibrium non-metal (oxygen) activity termed the dissociation activity. If the non-metal (oxygen) activity adjacent to the electrolyte ever becomes less than the dissociation activity, the electrolyte will begin to dissociate or decompose.

In the circulated pumping system described above, or in a stagnant system, the oxygen activity at the melt-/electrolyte interface must never be permitted to go below the dissociation activity. In a pumping system, a problem exists because oxygen is continuously being removed from the melt at the melt/electrolyte interface at a rate which is a function of the applied cell voltage, $E_{appl}$. Generally, an increase in $E_{appl}$ tends to increase the oxygen removal rate as represented by $i_{ion}$ in Eq. I.

As the applied cell voltage is increased, oxygen is transported away from the electrolyte/melt interface, through the electrolyte at an increased rate. If oxgyen is removed at a rate which decreases the oxygen activity at the interface to less than the dissociation activity, the electrolyte will begin to decompose. Similarly, of course if a constant voltage is applied to the cell, decomposition would occur if the rate of oxygen supply from the melt is inadequate to maintain the oxygen activity at the interface at or above the dissociation activity.

The decomposition concept may be quantitatively understood by reference to Eq. I. If $P_{O_2}$ is made equal to the dissociation activity for the electrolyte, then $E_{appl}$ and $i_{ion}$ become interrelated critical factors in decomposition.

If oxygen can only be supplied to the melt/electrolyte interface at a rate corresponding to a given $i_{ion}$, Eq. I (with the dissociation activity inserted) would give a maximum $E_{appl}$ termed $E_{max}$. Any voltage above $E_{max}$ would deplete the interface oxygen activity below the dissociation activity and cause decomposition of the electrolyte.

Similarly, for a given $E_{appl}$ there exists an $i_{ion\,min}$. If oxygen can not be supplied from the melt to the interface at a rate at least equal to $i_{ion\,min}$, an insufficient supply of oxygen will result in a depletion of oxygen activity at the interface and cause decomposition.

Therefore, from all of the above, it can be seen that for a given $E_{appl}$, oxygen must always be supplied at a sufficient rate to entirely supply $i_{ion}$ in equation I and bring it into balance.

In a stagnant system, $i_{ion}$ quickly approaches zero because transport in the bulk liquid is limited by diffusion which is relatively slow. Therefore, Eq. I quickly gives an $E_{max\ stagnant}$ which for example may be 2 volts.

We have discovered that by using the circulation shown in FIG. **1**, with a pumping voltage at or below the $E_{max}$ for a stagnant system, the deoxidation rate is significantly increased above that for a system limited by the rate of oxygen diffusion in the bulk liquid. Even more importantly, we have discovered that by circulating the melt as described above, the cell pumping voltage is not limited to the $E_{max\ stagnant}$. We may use pumping voltages far in excess of $E_{max\ stagnant}$ and thereby even more significantly increase the rate at which oxygen is removed from the melt.

FIGS. **4** and **5** illustrate the edeoxidation of a stagnant or uncirculated melt. In FIG. **4**, the curve **30** shows a very slow reduction in oxygen concentration in a liquid metal. Similarly in FIG. **5**, curve **32** shows that such a stagnant melt system provides a relatively small ionic deoxidation current. These curves were derived from experimentally verified equations.

We have discovered that by stirring the melt, especially by inductive stirring, the deoxidation rate can be greatly increased even at a pumping voltage at or below $E_{max}$. For example, FIG. **4** illustrates at curve **34** the reduction of oxygen concentration in such a system. FIG. **5** illustrates at curve **36** the ionic deoxidation current $i_{ion}$ as a function of time for such a system. These curves were also derived from experimentally verified equations.

Additionally, we have discovered that the circulation or stirring of the liquid metal permits the pumping voltage applied to the cell to be raised very substantially above $E_{max\ stagnant}$. This is permissible because stirring continuously supplies melt of higher oxygen concentration to the boundary layer region at the electrolyte wall and sweeps away oxygen depleted melt. Consequently, an adequate supply of oxygen atoms is continuously supplied to the melt/electrolyte interface. This adequate supply maintains the entirety of the ionic current $i_{ion}$ so that the electrolyte will not decompose even with voltages above $E_{max}$.

Therefore, initially at least, we have eliminated diffusion of oxygen atoms in the liquid metal as a factor retarding the deoxidation rate. So long as oxygen can be supplied to the interface at a sufficient rate, the very high cell pumping voltage may be maintained. In principle, for example, it may be even 100 volts. FIG. **4** illustrates, at curve **40**, the reduction of oxygen concentration for such a system having the pumping voltage above $E_{max\ stagnant}$. FIG. **5** illustrates at curve **42** the deoxidizing pumping current which occurs in this same system. Curves **40** and **42** are derived from experimental data as described below. A comparison of these three curves in both FIG. **4** and FIG. **5** illustrates the improvement provided by the present invention.

As oxygen is removed from the bulk liquid metal, the rate of supply of oxygen atoms to the boundary layer next to cell wall will be reduced because the concentration of oxygen in the bulk is reduced. Consequently, it ultimately will be necessary to reduce the applied pumping voltage and thereby $i_{ion}$ as concentration is reduced. Otherwise, electrolyte decomposition would become possible. The pumping rate must be reduced so that the rate at which oxygen ions are pumped through the electrolyte never exceeds the rate at which oxygen can be brought to the mlet/electrolyte interface by the circulating melt. Of course, as the concentration of oxygen in the liquid metal is reduced and therefore the oxygen supply rate at the interface region approaches the transport rate through the electrolyte, the pumping rate becomes increasingly dependent upon the transport rate to the interface. On the contrary, at high oxygen concentration, with an over-abundant supply of oxygen atoms to the vicinity of the melt/electrolyte interface, the pumping rate is limited chiefly by the ionic resistance $\Omega_{ion}$ of the solid electrolyte.

Therefore, the deoxidation rate is maximized by controlling the applied voltage of the power supply **18** so that the pumping rate or the ionic current $i_{ion}$ is always as great as possible but not in excess of the transport rate of oxygen atoms to the melt/electrolyte interface. As oxygen atoms are brought to the melt/electrolyte interface at a lower rate, the pumping voltage is re-

duced to reduce $i_{ion}$ in the cell. Such a reduction in pumping voltage may be accomplished for example with the control means illustrated in FIG. **1.**

Ideally, the control means would continuously monitor the oxygen activity at the melt/electrolyte interface. It would be a feedback system which would maintain the $E_{appl}$ high enough that the oxygen activity at the interface sufficiently exceeds the dissociation activity. As the interface activity approached the dissociation activity, it would reduce the voltage.

Unfortunately, any measuring probe would disturb the system and therefore give inaccurate readings. Therefore as an alternative, the bulk oxygen activity may be monitored by the probe **28** or **28A**. When such a probe indicates that the oxygen activity in the bulk is approaching an experimentally established percentage of the dissociation activity (e.g. $10^6 \times$ dissociation activity) the pumping voltage will be suitably decreased.

Alternatively FIG. **5** shows by curves **36** and **42** that the ionic pumping current $i_{ion}$ through the power supply stays constant for an initial time interval and subsequently decreases. The downwardly sloping curve results from a decreasing bulk oxygen activity. The total cell current is made up of the useful $i_{ion}$ plus electronic conduction. The ionic current integrated in time represents the oxygen removed and can therefore indicate the remaining oxygen content.

Consequently, the control means may be programmed to reduce the pumping voltage when the total current drops below an experimentally determined percentage of its initial constant value. This reduction may be done in steps. Each voltage reduction will be followed by an initially constant current and a subsequent decrease in current.

The above described methods and apparatus may also be used in other stages of the metal refining process. In a batch process, the power supply polarity may be reversed so that oxygen may be pumped from the ambient air into the liquid metal.

Introducing oxygen will allow carbon and sulphur impurities to combine with the oxygen and escape as CO and $SO_2$. After this is completed, the polarities are again reversed to pump oxygen out of the liquid metal.

The principles of the invention herein described are particularly advantageously applicable to a continuous casting process. In a continuous casting process, liquid metal is fed from a reservoir into a watercooled mold or caster where it solidifies. The solidified metal is continuously withdrawn from the mold and subsequently may be processed into appropriate shapes and lengths.

A deoxidation device such as illustrated in FIG. **2** may interposed in the continuous process between the metal reservoir and the caster. Although a single deoxidation stage is illustrated in FIG. **2,** it should be appreciated that several such stages may be serially connected. As will be apparent, the first such stage into which the liquid metal is introduced may have a substantially higher voltage than subsequent stages because the oxygen concentration is highest at the first stage. Each subsequent stage in turn may have a reduced voltage lower than the former stage. The voltage of each stage may be maximized so that an adequate supply of oxygen atoms is always available at all of the cell walls.

The staging can also be accomplished with a single set of tubes as shown in FIG. **2** by the use of several separate electrode bands inside the electrolyte tubes. Progressively, higher voltages would be applied to the individual cells at the upstream (high oxygen) end of the tubes.

The embodiment of FIG. **2,** has an outer tubular conduit **50** for containing the liquid melt stream as it is fed from the reservoir to the caster. An induction heater coil **52** similar to that illustrated in FIG. **1,** surrounds the conduit **50.** The electrochemical pumping cells comprise a plurality of tubular, electrolyte cells longutidinally aligned and distributed in the stream to form an oxygen pump. These tubular cells, **54, 56, 58** and **60** each have a tubular inner electrode (or set of electrodes) such as the inner electrode **70** in tubular cell **58.** The inner electrode **70** and inner electrodes in each of the tubular electrolyte cells may be constructed of the same material described in connection with the electrode **14** in FIG. **1.** The outer electrode is of course formed by the liquid metal **62** within the conduit **50** for each of the tubular electrolyte cells. The interiors of each of the tubular electrolyte cells must be supplied with an oxygen receiving fluid such as air and must be sealed from the flowing liquid metal usually by the use of closed-end tubes. Consequently, the open end of each tube extends through the plate **51** and is vented to atmosphere.

The operation of the embodiment illustrated in FIG. **2** is analogous to the operation of the embodiment in FIG. **1.** However, in the embodiment of FIG. **2,** the liquid metal is circulated not only by means of the induction of the heater coil **52** but further by the flow of liquid metal through the conduit **50.** Heating and stirring means other than the induction heater coil **52** may be used.

For example, a rotating magnetic field might be induced around the conduit **50.** A winding similar to the armature winding of an induction motor would cause a stirring of the melt.

Alternatively, the liquid metal could be circulated with sufficient tubulence if suitable mechanical means were interposed in the melt stream and additionally the effective total cell surface area were increased, for example by using a greater number of smaller tubes. In any case, it is necessary to sufficiently turbulently circulate the liquid metal so that the stagnant melt conditions illustrated at curves **30** and **32** in FIGS. **4** and **5** are avoided.

## EXAMPLES

An experimental example was performed with an apparatus similar to that illustrated in FIG. **1.** The liquid metal was copper having initially about 1000 parts per million oxygen. The crucible was partially stabilized zirconia plus 3–3 weight per cent CaO having a 2 inches outside diameter and a 1 13/16 inches inside diameter. The crucible had a total height of **6** inches and was coated on the external wall with a porous platinum electrode from the bottom so as to match the height of the liquid metal operating as the inner electrode. To effect a low resistance along the electrode exterior, between three and six layers of platinum paste were used, each layer being heated to 815°C prior to the application of the succeeding one. Carefully machined 2400°F fire bricks were used to insulate the electrolyte crucible and thus minimize the heat shock during melting of the metal. The fire bricks in the cell were contained in an alumina crucible which protected the furnace and induction coil from molten metal in case of an electrolyte

fracture. The induction furnace used has a power range of 0–20 Kilowatts. The copper melt was heated to 1150°C.

The melt was protected from oxidation by highly purified argon gas contained above the liquid metal. Ambient air was slowly circulated over the external surface of the electrolyte crucible to insure a constant oxygen pressure at the reference electrode. The contact wire to the molten metal was Chromel having the approximate composition 10% Cr, 90%Ni and dissolution of this contact was negligible. A cell voltage of approximately 3 volts was applied to the cell electrodes. The oxygen concentration was monitored as a function of pumping time. The results of this experiment are illustrated at curves **40** and **42** in FIGS. **4** and **5.**

Although in the experiment a 3 volt pumping voltage was applied to the electrolyte cell, an initial pumping voltage of a 100 volts or more should be possible so long as oxygen atoms are supplied to the melt/electrolyte interface at a sufficient rate.

It is to be understood that while the detailed drawings and specific examples given describe preferred embodiments of the invention, they are for the purposes of illustration only, that the apparatus of the invention is not limited to the precise details and conditions disclosed and that various changes may be made therein without departing from the spirit of the invention which is defined by the following claims.

I claim:

**1.** An apparatus for the exchange of oxygen with a liquid metal, the apparatus comprising:

a. a solid electrolyte cell formed by a solid, oxygen ion conducting electrolyte wall having a first surface in contact with said liquid metal and its opposite surface exposed to an oxygen transporting phase and having an oxygen transmitting electrode on said opposite surface, said liquid metal operating as the other electrode of said cell;

b. electromagnetic induction means for turbulently stirring said liquid metal past said electrolyte; and

c. a DC power supply connected to said cell electrodes for applying a pumping voltage to said cell.

**2.** An apparatus according to claim **1** wherein said liquid metal is contained in a receptacle and a control means is connected to said DC power supply for reducing the applied potential at a selected performance of the deoxidation process of said liquid metal.

**3.** An apparatus according to claim **2** wherein the negative terminal of said power supply is applied to said liquid metal to pump oxygen out of said metal.

**4.** An apparatus according to claim **2** wherein

a. metering means is connected to said liquid metal for metering the oxygen concentration in said liquid metal and providing an output signal corresponding to said concentration; and

b. a computing and control circuit is connected to the output of said metering means and said DC power supply for maintaining said applied potential less than that known to induce electrolyte decomposition.

**5.** An apparatus according to claim **1** wherein said liquid metal is contained in a receptacle and said electrolyte wall forms at least a portion of said receptacle.

**6.** An apparatus according to claim **1** wherein

a. a conduit is provided for containing a stream of said liquid metal;

b. means is provided for causing said liquid metal to flow through said conduit; and

c. said cell comprises at least one tubular cell in said stream to form an oxygen pump.

**7.** An apparatus according to claim **6** wherein said flow inducing means comprises an induction heater for stirring and heating said liquid metal.

**8.** A method for the deoxidiation of a liquid metal comprising:

a. electromagnetically inducing said liquid metal to turbulently circulate past an oxygen ion conducting solid electrolyte pumping cell; and

b. simultaneously applying a pumping voltage to said pumping cell for electrochemically pumping oxygen out of said liquid metal.

**9.** A method according to claim **8** wherein said pumping voltage is reduced as oxygen is removed from said liquid metal.

**10.** A method according to claim **8** wherein the applied pumping voltage is greater than the maximum breakdown voltage at which electrolyte would otherwise begin to dissociate if insufficient oxygen were available in the adjacent boundary layer of said liquid metal.

**11.** A method according to claim **10** wherein said pumping voltage is initially high but is subsequently reduced as oxygen is removed from said liquid metal.

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