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[54] METHOD OF DEOXIDIZING STEEL

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[30] **Foreign Application Priority Data**

Aug. 8, 1968 Japan....................................43/55988

[52] **U.S. Cl.** ....**75/58,** 73/23, 75/53, 204/195 S
[51] **Int. Cl.** **C21c 7/06**
[58] **Field of Search** ....73/23; 75/53, 57, 58, 129; 204/195 S

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[57] ABSTRACT

In a steel manufacturing process an oxygen concentration cell is immersed in the molten steel bath, the maximum differentiated value of the electromotive force is detected and the detected maximum value is utilized as the control factor for adjusting the quantity of deoxidizing agent to be subsequently added into the molten steel bath.

4 Claims, 6 Drawing Figures

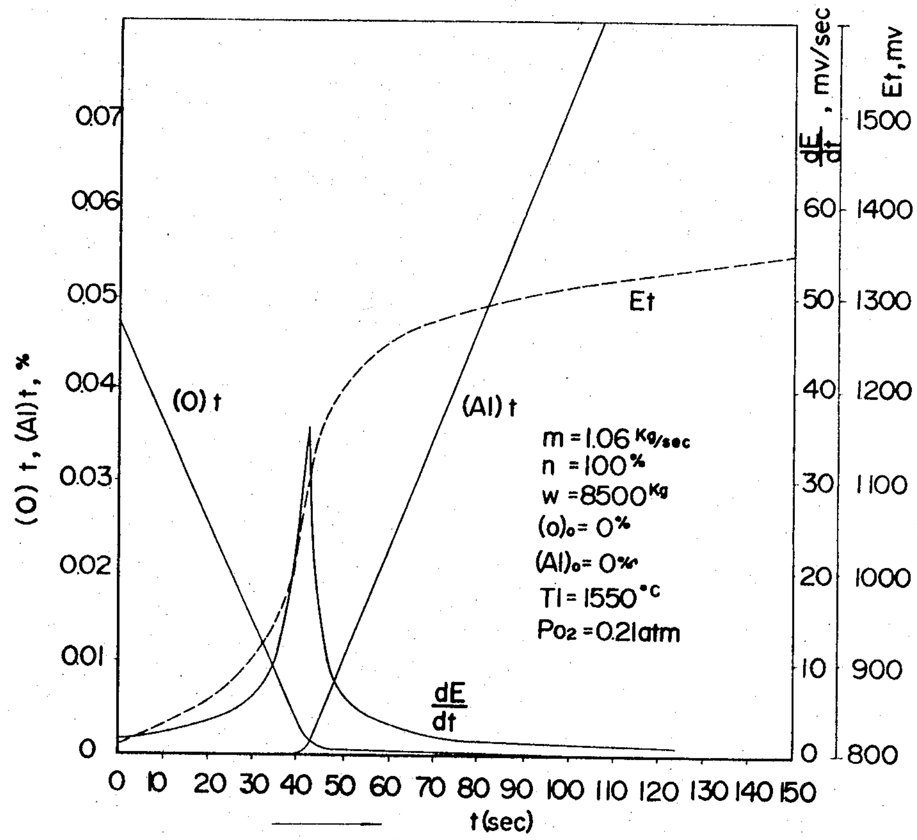
(O) t, (Al) t, %
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
$\frac{dE}{dt}$, mv/sec
60
50
40
30
20
10
0
Et, mv
1500
1400
1300
1200
1100
1000
900
800
Et
(O) t
(Al) t
$m = 1.06^{Kg/sec}$
$n = 100^{\%}$
$w = 8500^{Kg}$
$(o)_o = 0^{\%}$
$(Al)_o = 0^{\%}$
$Tl = 1550^{\circ C}$
$Po_2 = 0.21 atm$
$\frac{dE}{dt}$
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
t (sec)

FIG. 1

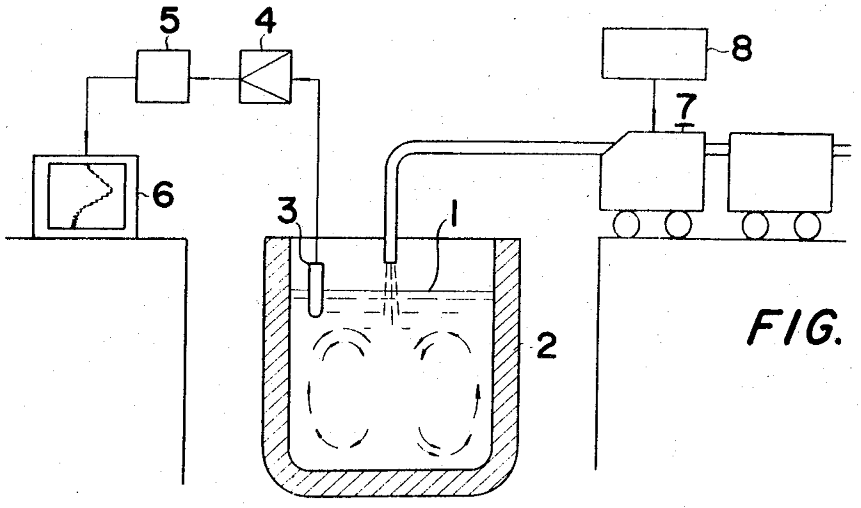

FIG. 2

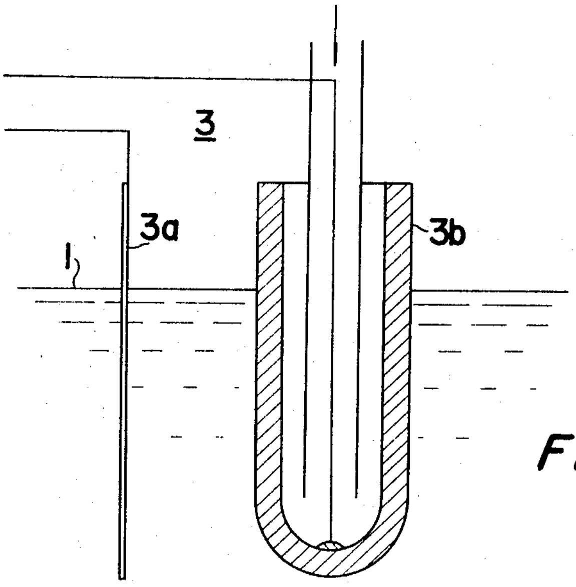

FIG. 3

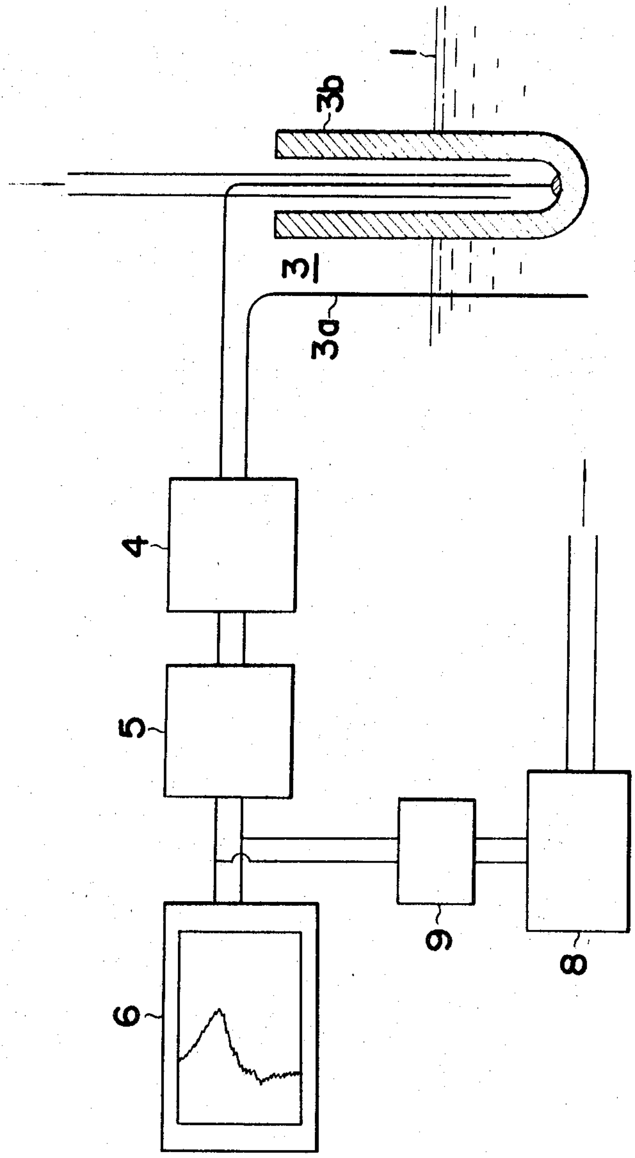

FIG. 4

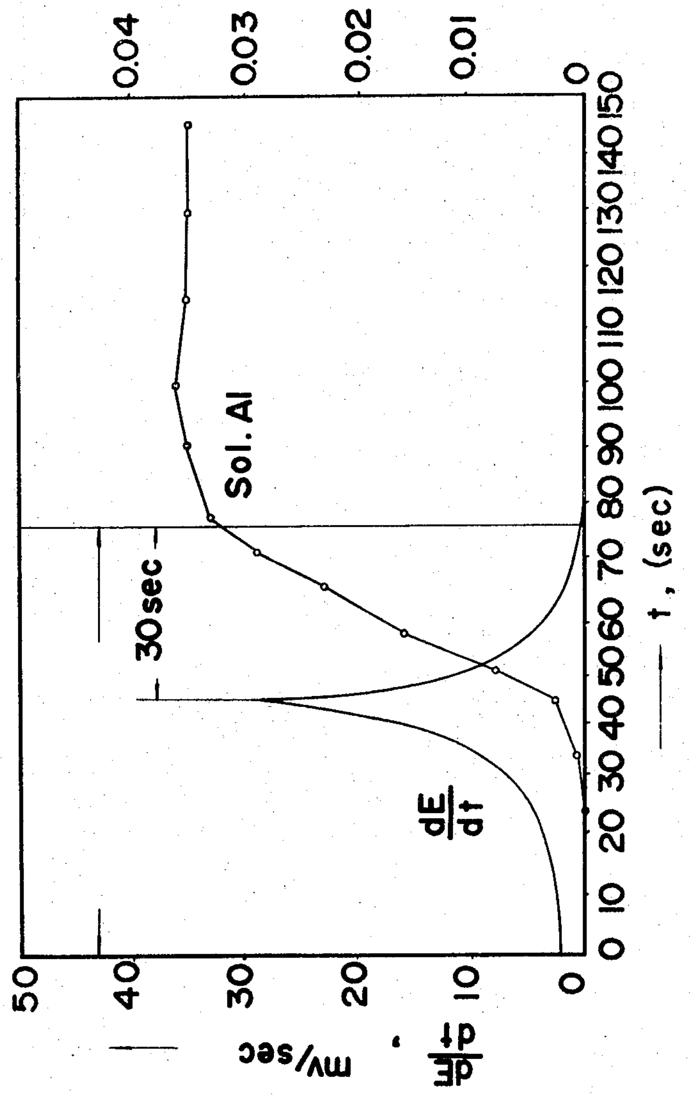
0
10
20
30
40
50
$\frac{dE}{dt}$, mV/sec
0
0.01
0.02
0.03
0.04
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
t, (sec)
$\frac{dE}{dt}$
Sol. Al
30 sec

FIG. 5

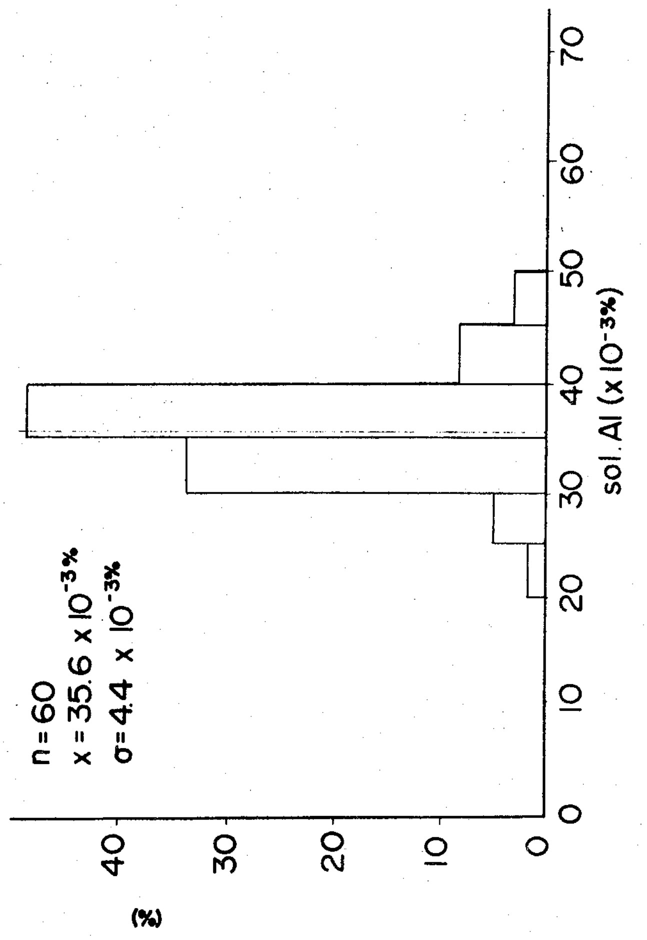
n=60
x = 35.6 x 10⁻³%
σ=4.4 x 10⁻³%
(%)
0
10
20
30
40
0
10
20
30
40
50
60
70
sol. Al (x 10⁻³%)

FIG. 6

METHOD OF DEOXIDIZING STEEL

BACKGROUND OF THE INVENTION

This invention relates to a method of manufacturing steel wherein the deoxidizing process of the molten steel is improved.

As is well known in the art, in the manufacture of steel, it is necessary to deoxidize molten steel before the casting process. Generally, such a deoxidizing treatment is performed by adding a suitable deoxidizing agent to the molten steel in a ladle, such as aluminum, aluminum alloys, manganese, silicon, calcium and magnesium. As the oxygen content of the molten steel is generally dependent upon the quantity of the deoxidizing agent, it is the common practice to add deoxidizing agent of a given weight per unit weight of said molten steel. With such a method of incorporation, however, the desired degree of deoxidation cannot be provided or the degree of deoxidation varies every heating owing to such disturbing factors as oxidation by the atmosphere at the time of teeming, oxidation with oxidizing slag, or the oxidation caused by the slag adhering to the inside wall of ladle. Thus, the control of the degree of oxidation is very difficult. Further, the control of adding said deoxidizing agent is also difficult and brings about final inequality of the added weight of said deoxidizing agent.

To eliminate such nonuniform degree of deoxidation, it has been the practice to sample a small quantity of said molten steel from the ladle, then to rapidly analyze the sample to determine the oxygen content in the molten steel so as to adjust the quantity of the deoxidizing agent to be added, or to preliminarily deoxidize in the furnace to stabilize the yield of the deoxidizing agent in the ladle. Further, it is well known that the deoxidizing agents are added into the ladle according to the so-called container method.

While these methods are able to make nonuniformity in the degree of deoxidation decrease to some extent, uniformity in the degree of deoxidation provided by these static and indirect methods is naturally limited as the above-described disturbing factors are difficult to measure. Thus, it has been impossible to greatly improve the uniformity in the degree of deoxidation.

Accordingly, it has been attempted to directly detect the degree of deoxidation of the molten steel in the ladle so as to control the quantity of deoxidizing agent to be added on the basis of the detected degree of deoxidation. To put this attempt into practice, it has been proposed to locate an oxygen concentration cell, such as stabilized zirconium-oxide electrolyte, in the ladle to determine the percentage of oxygen content in the molten steel. It is, however, well known that the method of determining oxygen content in the molten steel from the absolute value of the electromotive force of the above cell is not accurate and difficult to utilize. Especially, the measurement of the electromotive force is extremely difficult in a range of low oxygen contents in which sufficient deoxidation has been made. Thus, it is quite impossible to determine the degree of deoxidation from measured value. For this reason, until today no method has been practically realized according to the principle of the above-described method of manufacturing steel.

SUMMARY OF THE INVENTION

Accordingly, it is the principal object of this invention to provide a novel method of manufacturing steel capable of controlling the quantity of the deoxidizing agent in accordance with the degree of deoxidation of the molten steel, whereby it is possible to readily control the percentage of oxygen content in the molten steel as well as the percentage of the deoxidizing agent content dissolved therein, thus providing steel of high quality.

BRIEF DESCRIPTION OF THE DRAWING

Further advantages and objects of this invention together with the principal of operation can be readily understood from the following detailed description taken in conjunction with the accompanying drawing in which:

FIG. 1 illustrates theoretical characteristic curves helpful to explain the principle of this invention;

FIG. 2 diagrammatically represents an apparatus utilized to carry out this invention;

FIG. 3 is a diagram of essential components of the apparatus shown in FIG. 2;

FIG. 4 shows a modified embodiment of the apparatus utilized to carry out this invention;

FIG. 5 shows characteristic curves obtained by carrying out this invention; and

FIG. 6 is a statistical plot showing the soluble aluminum content of low-carbon aluminum-killed steels manufactured by the method of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention is based on the following theoretical considerations.

The theoretical calculation regarding the change in the electromotive force of the above oxygen concentration cell is as follows:

The material balance wherein aluminum is added at a constant rate, for t time and by a definite quantity is expressed by

$$\eta mt = W\left\{([A1]t-[A1]_0)+\frac{53.96}{48}([O]_o-[O]t)\right\} \qquad (1)$$

(2) Equilibrium relation balance A1 and 0

$$K'=(A1_t^{2}\cdot(O)_t^{3} \qquad (2)$$

(3) Relation between O and electromotive force

$$Et=\frac{-\Delta G^\circ}{\eta F}-\frac{R(Tl+273)}{nF}\,\mathrm{lm}\,\frac{[O]_t}{\sqrt{PO_2}} \qquad (3)$$

where m represents adding rate of A1,

t; adding time of A1,

η; A1 yield,

$[0]_o$; oxygen content of the molten steel before A1 addition,

$[O]t$; oxygen content of the molten steel after t time of A1 addition,

$(A1)_o$; A1 content of the molten steel before A1 addition,

$(A1)t$; A1 content of the molten steel after t time of A1 addition,

Et; electromotive force after t time of A1 addition,

Tl; Temperature percent of the molten steel,

K'; equilibrium constant,

ΔG°; standard free energy of the dissolved oxygen,

F; Faraday's constant and

n; charge number.

It is to be understood that these theoretical calculations were made where aluminum was used as the deoxidizing agent, where the molten steel was a static bath and where the effect of oxidation by the inside wall of ladle was neglected. Further, these calculations were based on the assumption that the equilibrium expressed by an equation $2A1+30 \rightleftarrows A1_2O_3$ holds true since the reaction rate can be considered very accurate.

Thus, by substituting value of m, η, W, $(A1)_o$, $(O)_o$, Tl and PO_2 in equations (1) (2) and (3), respectively, it is possible to obtain the relationship between (i) the aluminum content $(O)t$ in the molten steel after t time of A1 addition and A1 content $(A1)t$ of the steel bath, and (ii) the electromotive force Et of said oxygen concentration cell. Values of m=1.06 kg./sec.;η=100 percent, W=85,000 kg., $(O)_o$=0.047 percent, $(A1)_o$=0 percent, Tl=1,550° C., PO_2=0.21 atm. which are possible to be generally given were substituted in equations (1) (2) and (3) and the results of calculations were plotted as shown in FIG. 1. The abscissa represents the time t (seconds) while the ordinate shows oxygen content $(O)t$ (percent), aluminum content $(A1)t$ (percent), and differentiated value of electromotive force Et with respect to time dE/dt(mV/sec.). From FIG. 1 it was found that the differentiated value of the electromotive force with respect to time, that is, dE/dt(mV/sec.), reaches the maximum value when a predetermined quantity of aluminum is added in the molten steel as mentioned above, and when the oxygen content (O)t and aluminum content (A1)t reach a specific predetermined value (in the above example of calculation, (O)t 0.0016 percent, (A1)t 0.0005 percent). A similar phenomenon occurs when other deoxidizing agents than aluminum are used.

In this manner, it is evident that when the added time of A1, that is, adding quantity of A1, is limited to a predetermined value starting from the point which is the maximum differentiated value of the electromotive force in the oxygen concentration cell, both adjusting the content of Sol A1 to a desired definite value and controlling deoxidation rate to a desired definite degree are possible to be easily carried out.

In order that Sol A1 content and deoxidation rate of the molten steel is controlled to a desired value, the following equation (4) should be used wherein the time from the maximum differentiated value, that is, dE/dt, to the stopping point of adding A1 is possible to be calculation with ease.

$$\eta m(t'+t'')=W\left\{[(Al)t'-(Al)\ \max) + \frac{53.96}{48}[(O)\ \max-(O)t']\right\} \qquad (4)$$

where t' represents the time from the maximum differentiated value to the stopping point of adding A1, (A1)max, the aluminum content corresponding to the maximum differentiated value, (O)max, the oxygen content corresponding to the maximum differentiated value, (A1)t' the A1 content at the stopping point of adding A1, (O)t' the oxygen content at the stopping point of adding A1, η, the yield of added A1, and t'', the delay time.

The invention is characterized by immersing an oxygen concentration cell in the molten steel, detecting differentiated value of electromotive force in the cell while adding deoxidizing agent to the molten steel and adjusting the added quantity of the deoxidizing agent to a predetermined value after the maximum differentiated value has been reached.

Referring now to FIGS. 2 and 3, there is shown apparatus utilized to carry out this invention comprising a ladle **2** in which molten steel **1** is subjected to deoxidizing treatment, the molten steel having been subjected to preliminary deoxidizing treatment in the furnace. An oxygen concentration cell **3** serving as a detecting element for deoxidizing rate is immersed in the molten steel **1**. As shown in FIG. **3** the oxygen concentration cell **3** comprises a negative electrode **3***a* and a positive electrode **3***b* in the form of a bottom closed cylinder made of an electrolyte, the negative and positive electrodes are disposed in parallel and spaced apart a predetermined distance with thin lower ends immersed in the molten steel bath. Cooling gas such as air is introduced into the positive electrode **3***b*.

The electromotive force of the cell is amplified by a direct current amplifier **4** and then differentiated by a differentiating circuit **5**, the output thereof being recorded and displayed by a recording meter **6**. A container type device **7** is used to add an aluminum wire acting as the deoxidizing agent into the ladle **2** at a definite rate and by a constant quantity (e.g., 0.008 kg./sec. t). The start and stop operations of the supply device **7** are controlled by a time switch mechanism **8** which functions to automatically stop the supply device **7** after passing away of a specific time given by equation **4**.

The operation of the apparatus is as follows.

Molten steel **1** which has been made in a furnace and subjected, or not subjected, to the preliminary deoxidation treatment is tapped into the ladle **2** to a level sufficient to immerse therein the oxygen concentration cell **3**. Then supplying device **7** is started to add the A1 wire to the molten steel **1** at a predetermined speed and by a constant quantity. Simultaneously with the starting of supplying the aluminum wire the indicating recorder **6** is set into operation to record and display the differentiated value of the electromotive force in the cell **3** with respect to time.

When a predetermined interval has passed away after the starting of adding the aluminum wire, a rapid and large change takes place in the electromotive force of the cell **3**. In response to this change, the recording meter **6** will record and indicate the characteristic point, that is, the maximum differentiated value of the electromotive force with respect to time. Once this peculiar point is noted, the time switch mechanism **8** is immediately set into operation. Thus, the time switch mechanism will stop the operation of the supplying device after passing away of a further predetermined period of time. In other words, supply of the aluminum wire is ceased when it has been further added by a predetermined quantity. Then, the molten steel is poured into ingot mold and cooled to obtain ingots of the desired aluminum-killed steel.

FIG. **5** is a plot of the measured value of changes in the differentiated value dE/dt of the electromotive force in the oxygen concentration cell and in Sol A1 content of the above-described embodiment. The content of soluble aluminum was determined by analyzing the sample taken from the ladle during the course of adding the aluminum wire. From the result of measurement shown in FIG. **5** it was confirmed that at about 45 seconds after the start of adding aluminum wire the maximum differentiated value dE/dt was substantially coincident with said theoretical calculation. A predetermined time later (about 30 seconds) the incorporation of the aluminum wire was terminated to perform the desired degree of deoxidation. Further, it was possible to bring the Sol A1 content to the desired level (0.035 percent). Comparison was made between dispersion in Sol A1 content contained in the low-carbon aluminum-killed steel of a number of batches embodying this invention (Composition; C: 0.04 ~ 0.06 percent, Mn: 0.25 ~ 0.35 percent, P: 0.008 ~ 0.012 percent, S: 0.015 ~ 0.021 percent) and that of low-carbon aluminum-killed steel prepared by the conventional method wherein just before tapping the oxygen content of the molten steel was analyzed to adjust adding quantity of aluminum. FIG. **6** shows the result with the present invention, in which the abscissa represents Sol A1 content and the ordinate, frequency in percent. The method of this invention can reduce the range in dispersion of Sol A1 content, and moreover it is possible to lower the peak value. More particularly, with the method of the prior art the number of samples n was 1,432, the value of the center line $\bar{\chi}$ was $43.9\times10^{-}$percent, and the standard deviation δ was $10.5\times10^{-}$percent, whereas with the method of this invention, although the number of samples n was only 60, the value of the center line $\bar{\chi}$ was 35.6×10^{-3} percent, and the standard deviation δ was 4.4×10^{-3}, said center line being shown by dot and dash lines in FIG. **6**.

FIG. **4** illustrates a modified apparatus for carrying out this invention. Although in the previous embodiment the operation of the timer switch mechanism **8** was initiated manually, in this modification a relay **9** is added to actuate the time switch mechanism when the recording meter **6** displays said peculiar point of maximum dE/dt.

Thus, according to this invention, it is possible to assure a highly accurate control of the added quantity of the deoxidizing agent as well as higher quality of the steel.

Although in the above-described embodiments, the deoxidizing agent was added into the molten steel by a constant quantity and at a definite rate, and while such a method is advantageous, in certain cases, as far as the quantity can be controlled accurately, other adding means not including a timing mechanism can be used. Further, it is to be understood that the deoxidizing agent is not limited to aluminum wire, and that other various deoxidizing agents, as already pointed out, can also be used. Also the construction of the oxygen concentration cell is not limited to that illustrated in the drawing. Thus, it may be of any type so far as it can produce an electromotive force in response to the changes in the oxygen content in the molten steel.

In brief, according to this invention an oxygen concentration value is detected as a function of its electromotive force and the detected value is utilized as the controlling factor to adjust quantity of the deoxidizing agent to be added. Thus, more direct feedback control can be provided and the decreasing of steel-making time is possible to be expected when compared with the prior method wherein analysis is made during the steel-making operation to determine the required quantity of the deoxidizing agent to be added. Moreover, it becomes possible to perform effective controls for disturbing factors which heretofore have been impossible to measure. Thus, it is possible to substantially prevent nonuniformities in the deoxidizing rate and content of a deoxidizing agent, thus performing sufficient deoxidation as desired and confining the content of the deoxidizing agent to a definite low and narrow range. The low-carbon aluminum-killed steel prepared in accordance with this invention is suitable for use in deep drawing operation.

While the invention has been shown and described in terms of its preferred embodiments, many changes and modifications will be obvious to one skilled in the art within the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of manufacturing steel characterized by immersing an oxygen concentration cell in a molten steel bath, detecting the differentiated value of the electromotive force in said cell with respect to time while adding a deoxidizing agent into said molten steel bath, detecting the maximum value of said differentiated value of said electromotive force, and regulating the additional quantity of said deoxidizing agent to be added into said molten steel bath to a predetermined definite value after said differentiated value has reached said maximum value.

2. The method according to claim 1 wherein said additional quantity of said deoxidizing agent to be added after said differentiated value reaches the maximum value is controlled to a predetermined amount by a timer mechanism.

3. The method according to claim 2 wherein said maximum differentiated value is detected by a meter which sets said timer mechanism into operation responsive to the maximum differentiated value of said electromotive force being reached.

4. The method according to claim 1 wherein said additional quantity of said deoxidizing agent is regulated by adding said deoxidizing agent for a predetermined period of time after said maximum differentiated value is detected.

* * * * *