United States Patent

Grenfell

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[54] **MANGANESE CONTROL IN BASIC STEELMAKING PROCESS**

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[52] **U.S. Cl.** **75/60,** 75/59

[51] **Int. Cl.** **C21c 5/32**

[58] **Field of Search** 75/59, 60, 51, 52

[56] **References Cited**

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[57] **ABSTRACT**

The invention relates to the refining of steel and has particular reference to the refining of steel by a process in which a stream of hot gases is directed onto the upper surface thereof.

The invention particularly provides for a method of controlling the manganese content of the melt at turn-down of a steel refining process by at least a two stage process in which the refining is carried out using a gas stream comprising the products of combustion of a fuel and uncombined oxygen by varying the proportions of combustion products to uncombined oxygen in a first stage in which the gas stream is relatively poor in uncombined oxygen and in a subsequent or second stage in which the gas stage is relatively rich in uncombined oxygen and varying the duration of the first stage so that with a relatively long first stage a low manganese reversion is obtained and by providing a relatively short first stage a high manganese reversion to the melt at turn-down is obtained.

6 Claims, 3 Drawing Figures

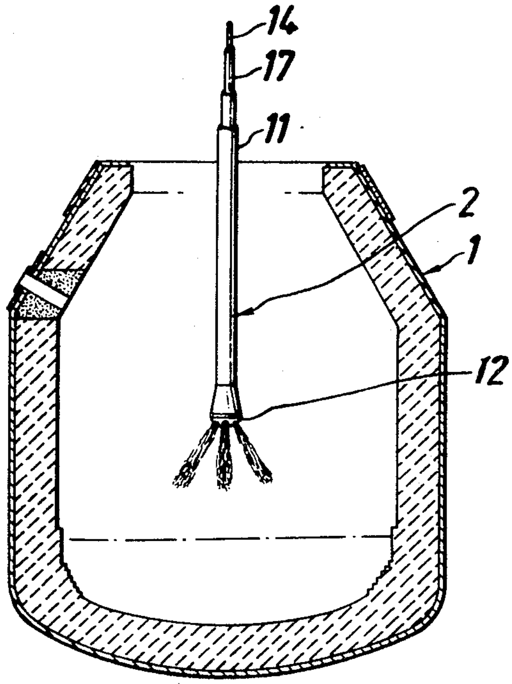
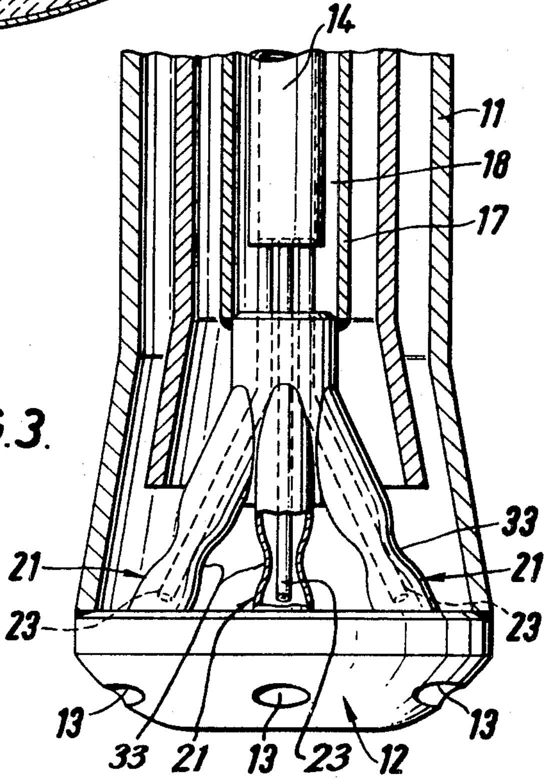


FIG. 2.

FIG. 3.



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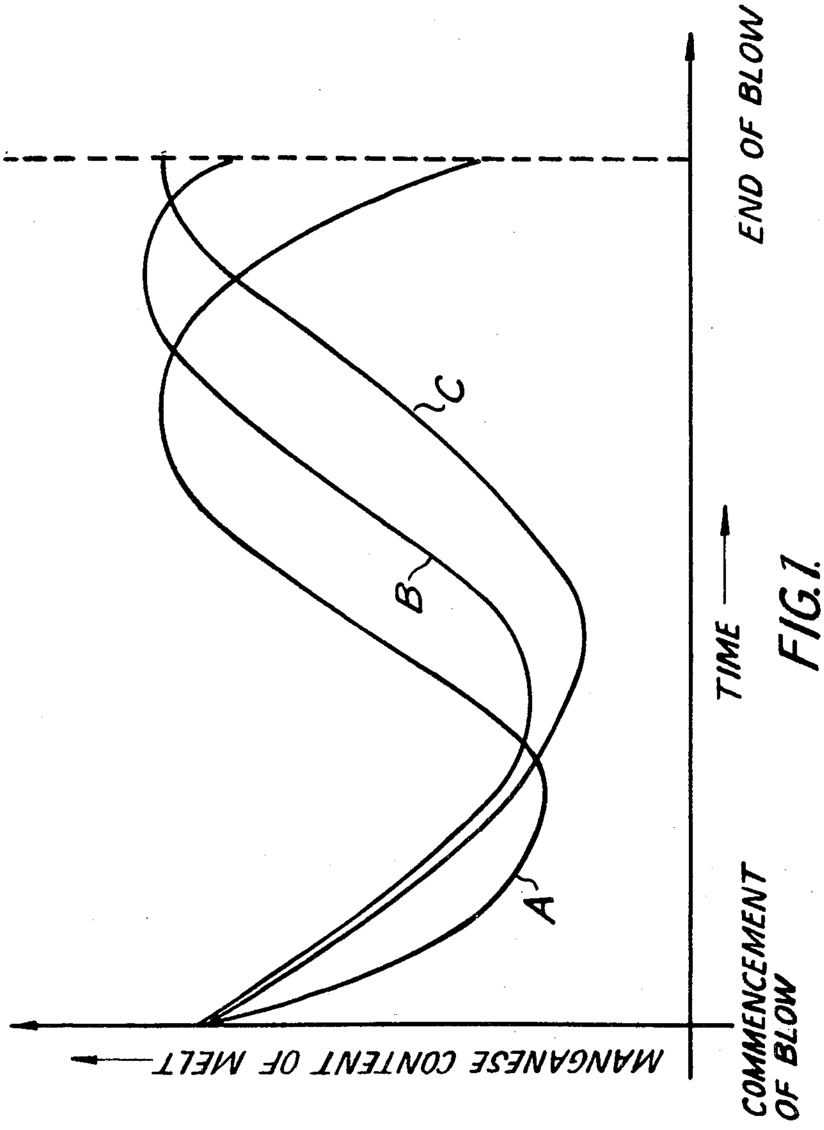

FIG.1.

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MANGANESE CONTROL IN BASIC STEELMAKING PROCESS

The present invention relates to an oxygen fuel process for the refining of crude iron to steel. The invention is concerned with the control of the manganese content in the melt at the "-turn-down" or end of such a process.

In steels for use in rolling a proportion of 0.30 to 0.40 percent manganese improves the rolling properties of the steel quite considerably. In conventional steel making processes, although crude iron frequently has fairly high concentrations of manganese, normal refining practises presently employed, typically L.D. practice, reduces the manganese content in the steel to substantially less than 0.15 percent by weight and the balance of manganese required has to be made up by the addition of ferro-manganese in the ladle. In view of the relatively high cost of ferro-manganese, it is desirable to control the amount of manganese retained in the melt so that where steels for use in rolling are to be produced, as high a manganese content as possible can be retained in the melt, to reduce the quantity of ferro-manganese necessarily added within the ladle.

Our co-pending application, Ser. No. 776,417, filed Nov. 18, 1968 describes and claims a process for refining a ferrous metal charge which process comprises subjecting the charge to a treatment with a stream of hot refining gas obtained by the combustion of a fuel in an excess of oxygen to provide a refining gas stream comprising the products of combustion together with uncombined oxygen, wherein the proportion of combustion products and uncombined oxygen is varied during the treatment to provide a first slag forming stage in which the gas is relatively poor in uncombined oxygen, a second decarburizing stage in which the gas stream is relatively rich in uncombined oxygen, and a third correction stage in which the gas stream is relatively poor in uncombined oxygen.

According to the present invention there is provided a process for controlling the manganese reversion of a ferrous metal charge during refining which process comprises subjecting the molten charge to a treatment with a stream of hot refining gases obtained by the combustion of a fuel in an excess of oxygen to provide a gas stream comprising the products of combustion and uncombined oxygen and varying the proportion of combustion products and uncombined oxygen in the refining gas stream in at least two stages to provide a first stage in which the gas stream is relatively poor in uncombined oxygen and a subsequent stage in which the gas stream is relatively rich in uncombined oxygen and varying the duration of said first stage so that by providing a relatively short first stage a high manganese reversion to the melt at turn-down is obtained and by providing a relatively long first stage a low manganese reversion to the melt at turn-down is obtained.

The present invention also provides a process for refining a ferrous metal charge to steel in a converter vessel by employing hot refining gases directed downwardly to the charge at high velocity from a nozzle fed by oxygen and fuel to provide a refining gas stream comprising combustion products and uncombined oxygen and varying the proportion of combustion products and uncombined oxygen in the refining gas stream in at least two stages which stages comprise a first slag forming manganese control stage in which the gas stream is relatively rich in combustion products and relatively poor in uncombined oxygen and a second or subsequent decarburizing stage in which the gas stream is relatively poor in combustion products but relatively rich in uncombined oxygen and varying the duration of said first stage so that by providing a relatively short first stage, a high manganese reversion to the melt at turn-down is obtained and by providing a relatively long first stage a low manganese reversion to the melt at turn-down is obtained.

A third stage constituting a regulating and terminal refining stage may be provided in which the gas stream is relatively rich in combustion products and relatively poor in uncombined oxygen. Typical fuels which may be employed are hydrocarbon fuels and in particular liquid hydrocarbons. It is preferred that the fuel is fuel oil, residual fuel oils being suitable.

Typically, the liquid fuel and oxygen may be fed to a burner-type lance having a nozzle which provides a flame surrounded by an oxygen rich envelope. The surrounding envelope substantially prevents uncombusted fuel from contacting the melt or reactive portions of the slag thereby preventing the introduction of fuel contained impurities into the charge. In operating the process it is possible to vary the proportion of products of combustion and oxygen in the refining gas streams by varying the oil flow and then maintaining the oxygen flow constant. Alternatively, the oil flow can remain constant and the oxygen flow can be varied. For practical purposes, however, it is preferred to maintain a constant oxygen flow and to vary the oil flow to provide the desired excess oxygen, since the availability of oxygen is usually a practical limiting factor.

Following is a description by way of example and with reference to the accompanying drawings of methods of carrying the invention into effect.

In the drawings:

FIG. 1 illustrates the variation of the manganese content of a melt during the course of typical blows;

FIG. 2 is a sectional view of an open top converter type vessel having a lance suitable for use in the process of the present invention;

FIG. 3 is a section through a preferred lance for use in the practice of the present invention.

In the process of the present invention an open top basic refractory lined converter vessel is charged with molten iron and solid scrap. A burner-type lance and mounting assembly is disposed with respect to the converter so that the lance is capable of being moved vertically into and out of the open top of the vessel as shown in FIG. 2. The lance has a delivery nozzle at one end through which fluid may pass. In the case of larger converters, for example 200 tons nominal capacity, the nozzle preferably has a plurality of discharge orifices positioned whereby fluids passing therethrough are directed generally downwardly and outwardly.

In smaller converters, for example 50 tons nominal capacity, a single-orifice lance is suitable.

Taking account of the factors hereinafter described, the pattern to be taken with the three stages of the process is established. The three refining stages will hereinafter be referred to for convenience as Stage I, Stage II and Stage III. The lance is purged with steam and is lowered to its initial operating position. The oxygen flow is started and as oxygen issues from the end of the lance, the steam purge is terminated and the fuel oil supply started. Ignition of the fuel oil is instantaneous and the melt ignition occurs almost immediately afterwards.

Slag forming materials may be part of the initial charge but usually are added to the charge 1 or 2 minutes after ignition. The slag-forming materials may be, e.g., lime, limestone, dolomitic lime or mixtures thereof.

The first slag of the process is essentially a slag-forming and preliminary refining stage in which the control of the manganese reversion in the melt is effected. During this stage, streams of high purity oxygen and liquid carbonaceous fuel are flowed to the burner lance in proportions to produce a stream of hot gas relatively rich in combustion products and relatively poor in uncombined oxygen.

It is thought that during the course of the process, the manganese content of the melt follows the general form of the curves shown in FIG. 1 of the accompanying drawings. It will be noted that during the blow the manganese content of the melt is first reduced to a minimum and manganese is abstracted from the melt and enters the slag. As the flow proceeds, a manganese reversion occurs whereby manganese leaves the slag and re-enters the melt. This reversion rises to a peak towards the end of the blow and then begins to reduce as the manganese is again abstracted from the melt by the slag.

By providing a long initial first stage, the slag forms and becomes hot relative to the melt and manganese is abstracted from the melt and enters the slag quickly so that the minimum manganese content in the melt is reached as quickly as possible. As the melt temperature increases, manganese re-enters the melt from the slag and a proportion of manganese in the melt increases to a peak after about two-thirds of the blowing time and thereafter reduces as the temperature of the melt increases towards the turn-down temperature so that at the end of the blow the amount of manganese within the melt is quite low.

With a short first stage, the slag is comparatively cool as formed, and the manganese is retained in the melt very much longer so that the minimum quantity of manganese within the bath is reached at a much later time in the blow than in the case where a relatively long first stage blow is employed. Thereafter, the manganese reversion occurs with the manganese re-entering the bath from the slag so that the manganese content of the bath due to reversion reaches a peak just before termination of the blow so that very little manganese is abstracted from the bath by the slag prior to turn-down and teeming of the melt. In consequence, the proportion of manganese within the bath at this stage is very much higher.

By the term "relatively short first stage" is to be understood a first stage blow having a duration sufficient to form a cool slag so as to retard the abstraction of manganese from the melt in the early part of the blow thereby delaying the reversion peak until towards the end of the blow thereby resulting in a melt having, at turn-down, a comparatively high manganese content when considered in comparison with a normal blow using pure oxygen. A typical period for a short first stage is 4 to 6 minutes.

By the term "relatively long first stage" is to be understood a stage having a duration sufficient to form a hot slag to result in the rapid abstraction of manganese from the melt so that the minimum manganese content is reached early in the refining process thereby permitting the reversion to occur as the temperature of the melt rises so that the reversion peak is attained substantially before the end of the blow thereby resulting in a reduced manganese content in the melt at the turn-down. A typical period for a long first stage is 8 to 10 minutes.

By the term "relatively rich in combustion products" it is not necessarily intended that a major proportion of the refining gas in Stage I of the process comprises combustion products though that may be the case. Rather it is intended that the term connote relativity to the composition of the refining gas in the second stage of the process.

During Stage I, oxygen is flowed to the lance in a quantity in excess of that required for complete combustion of the fuel, thereby providing uncombined oxygen in the refining gases employed in that stage. The excess oxygen flowed to the lance in Stage I, while small when compared to the excess employed in Stage II, ensures complete combustion of the fuel, minimizes the danger of introduction of fuel-contained impurities into the charge, and provides uncombined oxygen for preliminary refining. The excess is not so great as to initiate a vigorous early carbon boil as in the L.D. process. Rather, the hot refining gases of the process are oxygen-starved relative to L.D. refining gas (undiluted, pure oxygen) and the typical early refining reactions of silicon and carbon therefore proceed at a greatly reduced rate. The hot gases, typically 4,000° - 5,000° F. in this stage, aid in fluxing the slag making materials to provide a reactive fluid slag within the first few minutes of Stage I. Thus a reactive basic slag is formed in the process in advance of excessive acid silica formation, thereby reducing silica attack of the converter's basic refractory lining. The foregoing is in contrast to the autogeneous L.D. process wherein slag development is dependent upon heat produced by exothermic refining reactions of cold oxygen with impurities in the crude iron charged to the converter.

It has been determined that for oxygen supply rates and fuels of the character employed in the appended examples, the excess may be within the range 25 to 300 percent in excess of the quantity of oxygen theoretically required for complete combustion of the fuel. It is preferred that an oxygen excess of 50 to 150 percent is employed and typically an oxygen excess of 60 to 70 percent is employed. An excess of uncombined oxygen in Stage I greater than about 300 percent results in relatively poor slag-making and bath-conditioning since a cooler flame is obtained in the higher excess range and also since higher excesses cause excessive refining reactions, especially silicon reactions, at a point too early in the process. An excess of less than 25 percent results in unnecessary lengthening of refining time, resulting in poor heat transfer efficiency of the oil burnt. Additionally, the low excess can cause a high percentage of iron oxide to remain in the slag, thereby decreasing the yield due to a "soft" blow. However, the preferred excesses may vary in the case that there is employed in the process a fuel of substantially different heating value and/or an oxygen supply rate substantially different from those as discussed in the examples.

The hot gases issuing from the flame at the lower end of the lance, typically at a temperature of 4,000° to 5,000° F., in Stage I are usually themselves sufficient to flux the slag making material without the use of conventional fluxing agents. Conventional fluxing agents, such as fluorspar or millscale may however be added to further accelerate formation of the fluid slag and to assist in the early phosphorus removal in the process as explained hereafter.

In addition to manganese control, in Stage I of the process, the FeO content of the slag is still quite high since the bath is relatively cool and this condition lends itself to the early removal of phosphorus and sulphur from the bath. Some carbon and silicon is also refined in Stage I although major carbon refining is delayed until a later stage in the process.

Stage II of the process is the stage in which the major decarburisation of the melt takes place. During this stage, the refining occurs using a high excess of uncombined oxygen over that required to effect complete combustion of the fuel and typically the excess is within the range of 1,000 to 1,300 percent. Where the fuel is a liquid carbonaceous fuel such as fuel oil, it has been found expedient to maintain the oxygen flow and to reduce the fuel supply to the lance to the desired level. The great excess of oxygen in Stage II initiates a vigorous carbon boil in the melt and the major portion of the carbon refining in the process occurs during this stage. The hot refining gas stream issuing from the burner type lance at this stage of the process comprises 90 to 95 percent by weight of hot uncombined oxygen directed by means of discharge orifices or nozzles of the lance towards the charge at high velocity. The hot gases, typically at a temperature of the order of 2,500° to 3,000° F. issue from the nozzles in the lance and assist in maintaining the slag fluid by preventing slag cooling or chilling, which can occur in the L.D. process where cold oxygen alone at a temperature of −150° F. is blown onto the charge.

The duration of Stage II is generally within the range 8 to 15 minutes, more or less, depending for example upon the desired carbon and temperature end points. Also, the Stage II duration is dependent on the proportion of scrap included in the charge. In general the higher the proportion of scrap in the charge, the shorter the duration of Stage II.

Where a three-stage process is employed, the stage III is a terminal refining and regulating stage which serves to control as far as possible the end point temperature and the carbon content. This control is effected by increasing the proportion of combustion products in the refining gas stream so that the excess of uncombined oxygen over that required to effect complete combustion of the fuel is generally 25 to 200 percent. The duration of Stage III is controlled principally by the need to ensure that the required total amount of fuel is employed during the process. In a typical operation, the desired turn-down temperature is of the order of 1,600° C. This temperature may be controlled by the amount of scrap incorporated in the charge and by the total amount of oil needed to be supplied to the refining vessel during the blow to effect heating of the charge. The duration of the final stage when employed is typically 5 to 16 minutes.

The total refining time of the process of the present invention is generally 20 to 30 minutes, but this can be varied as necessary or desirable and depends to a degree on available oxygen capacity of converter vessel, fuel characteristic and lance characteristics. Generally, the greater the oxygen availability, the shorter will be the overall refining time.

A variety of nozzles or lances may be employed in the practice of the present invention and variations will be apparent to the man skilled in the art. In the refining stages streams of hydrocarbon fuel, preferably a liquid carbonaceous fuel, and substantially pure oxygen are, in proportions defined above, flowed to the burner-type lance and contacted therein to form a fuel-oxygen stream. The fuel-oxygen stream is ejected from the lance, preferably at supersonic velocity to eliminate or reduce turbulence in the stream. Turbulence in the streams is generally to be avoided since a non-turbulant stream is important for effectively delivering the hot refining gases to the charge being refined. The radiant heat from the vessel walls and charge is sufficient to cause ignition to produce a flame (c.f. FIG. **2**) extending from the discharge orifices of the lance. The hot refining gases emitting from the flame comprise combustion products and uncombined oxygen and are directed generally downwardly and outwardly from the lance toward the charge at a high velocity.

It has been found, however, that a lance having the general nozzle arrangement shown in FIG. 3 of the accompanying drawings is especially suitable. The lance comprises an elongate body member **11** which is provided with a combined delivery and burner nozzle **12** at the lower end thereof. The interior of the body member **11** of the lance is built up with a number of annular passageways and conduits by which oxygen and liquid fuel are supplied to a plurality of discharge orifices **13** formed in the combined delivery and burner nozzle **12**. The number of nozzles is determined to some extent by the size of the refining vessel. With small vessels a single nozzle lance has been found to be suitable but for commercial size operation with converters of 200 and 300 ton capacity, a lance having three or four discharge orifices **13** and a burner nozzle **12** would be suitable. A fuel oil supply conduit comprising a pipe **14** is preferably located centrally of the body member **11** of the lance **10**. A plurality of pipes **16** are welded at **15** to the lower end of the pipe **14** and extend downwardly therefrom the pipes **16** corresponding in number to the number of discharge orifices **13**, and the plurality of oxygen supply pipes **21** disposed at an angle to the longitudinal axis of the lance and incorporate means such as venturi **33** for accelerating the oxygen. The fuel supply conduit is preferably provided with an annular jacket disposed between the oil conduit and the oxygen supply conduit to insulate preheated fuel in the fuel supply conduit. This is necessary since when using heavy grades of fuel oil, the low temperature of the oxygen passing down the oxygen supply conduit **18** chills the oil and may prevent oil flow.

Fuel supply conduit **14** is provided at its outlet end with a plurality of fuel supply pipes **23** extending therefrom and each having its end portion secured in the corresponding oxygen supply pipe **21** so that oxygen flowing through said supply pipes to the discharge orifices will flow in an annulus around the end of the corresponding fuel supply pipes whereby fuel will be entrained in the oxygen supplies when discharged from the discharge orifices.

The lance nozzle arrangement provides for the entrainment of fuel in a substantially pure stream of oxygen and when ejected from the lance nozzle will ignite to provide a short flame surrounded by a sheath-like envelope rich in uncombined oxygen. This arrangement ensures that during the refining process the products of combustion but not the flame itself is in contact with the melt and with the slag thereby preventing contamination of the melt with fuel-contained impurities such as sulfur. The avoidance of charge-contamination with such impurities is generally important in the process of the invention.

The following comparative examples serve to illustrate the process of the present invention.

EXAMPLE 1

This is an example of pure oxygen blow and is not in accordance with the invention.

A charge comprising 100 lbs. of scrap, 1,000 lbs. of hot metal and 40 lbs. of lime were added to a top blown converter. A single orifice lance having a nozzle construction as described above was introduced into the mouth of the vessel and pure oxygen was supplied to the lance for a period of 24 minutes at a rate of 3,200 cubic ft. of oxygen.

The hot metal temperature at the start of the blow was 1,350° C. and the finishing temperature was 1,600° C. The quantity of FeO in the slag was 20.5 percent.

Table I illustrates the comparison of hot metal and finishing steel analyses.

TABLE I

	Hot Metal Analysis	Finishing Steel Analysis
Carbon	4.30	**0.045**
Manganese	0.8	**0.10**
Phosphorus	0.9	**0.009**
Sulphur	0.035	**0.012**
Silicon	0.8	Nil

EXAMPLE 2

This example is an example in accordance with the present invention to obtain a low manganese figure in the finishing steel analysis.

An open top converter vessel was charged with 200 lbs. of scrap, 1,000 lbs. of hot metal and 40 lbs. of lime. The hot metal temperature was 1,350° C.

The charge was blown with fuel oil and oxygen using a single orifice lance as described above. The fuel oil was a gas oil and the blowing practice was a first stage of 10 minutes at a fuel oil flow of 12 gallons per hour and an oxygen flow of 5,600 cubic ft. per hour, a second stage of 8 minutes at a fuel oil flow of 2 gallons per hour and an oxygen flow of 5,600 cubic ft. per hour and a final stage of 6 minutes at a fuel oil flow of 12 gallons per hour and an oxygen flow of 5,600 cubic ft. per hour. The total blowing time was, therefore, 24 minutes. The finishing temperature was 1,610° C. and the quantity of FeO in the slag was 23 percent.

Table II sets out a comparison of the hot metal analysis and finishing steel analyses.

TABLE II

	Hot Metal Analysis	Finishing Steel Analysis
Carbon	4.30	**0.05**
Manganese	0.9	**0.04**
Phosphorus	1.1	**0.006**
Sulphur	0.04	**0.015**
Silicon	0.80	Nil

It will be noted that by providing a relatively long first stage to the process i.e., of the order of 10 minutes the manganese content was reduced from 0.9 percent in the hot metal to 0.04 percent in the finished steel.

EXAMPLE 3

This example is a repeat of Example 2 to illustrate the practice to obtain a high manganese yield in the finishing steel analysis.

The converter used in Example 2 was charged with 200 lbs. of scrap, 1,000 lbs. of hot metal and 40 lbs. of lime. The hot metal temperature was 1,370° C. The charge was blown for a period of 24 minutes using fuel oil and oxygen by the process comprising a first stage of 5 minutes at a fuel oil flow of 12 gallons per hour and an oxygen flow of 5,600 cubic ft. per hour, a second stage of 8 minutes at a fuel oil flow of 2 gallons per hour and oxygen flow of 5,600 cubic ft. per hour and a third and final stage of 11 minutes at a fuel oil flow of 12 gallons per hour and an oxygen flow of 5,600 cubic ft. per hour.

The finishing steel temperature was 1,615° C. and the proportion of FeO in the slag was 21 percent.

Table III is a comparison of the hot metal analysis with the finishing steel analyses.

TABLE III

	Hot Metal Analysis	Finishing Steel Analysis
Carbon	4.10	0.05
Manganese	0.8	0.22
Phosphorus	0.9	0.007
Sulphur	0.04	0.017
Silicon	0.90	Nil

It is clear from the table above that the manganese content of hot metal has been reduced far less than that of Example 1.

The diagram of FIG. 1 illustrates the manganese content during the course of the blow. Curve B is the variation of the manganese content of the melt with time during the course of the blow using pure oxygen as in Example 1 above. Curve A illustrates the variation of the manganese with time during the blow in which a long first stage is employed as in Example 2 and Curve C is a similar curve in which a short first stage is employed as in Example 3. It will be noted that the final peak of Curve C is very much later than that of either of Curves A and B and that as a result the proportion of manganese in the melt at the termination of the blow is very much greater. It will be appreciated that by selecting a suitable duration for the first stage, the proportion of manganese within the melt at turn-down can be controlled quite accurately.

I claim:

1. In a basic steel making process wherein a molten charge is subjected to hot refining gases produced by the combustion of fuel in excess oxygen the proportions of which are varied in at least two stages to provide a first stage high in combustion products and low in uncombined oxygen and a second stage low in combustion products and high in uncombined oxygen, the improvement in combination therewith comprising a method for controlling the manganese reversion to the melt at turndown by regulating the length of time of said first stage to provide high and low manganese reversion by short and long first stages, respectfully.

2. The method of controlling the manganese reversion set forth in claim 1 wherein said first stage comprises the formation of a slag and said second stage provides the major decarbonization of the melt.

3. The method of controlling the manganese reversion set forth in claim 2 wherein maximum manganese reversion is provided by regulating the time of said first stage to obtain a cool slag formation and wherein minimum manganese reversion is provided by regulating the time of said first stage to obtain a hot slag.

4. The method of controlling the manganese reversion set forth in claim 1 wherein said refining process includes a third terminal refining and correction stage wherein the gas stream is low in uncombined oxygen and high in combustion products.

5. The method of controlling the manganese reversion set forth in claim 1 wherein said refining process, said first stage includes an excess of from about 25 to 300 percent oxygen of that theoretically required for complete combustion and said second stage includes an excess of about 1,000 to 1,300 percent required for complete combustion.

6. The method of controlling the manganese reversion as set forth in claim 1 wherein said first stage is from 8 to 10 minutes for minimum manganese reversion and 4 to 6 minutes for maximum manganese reversion.

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