METHOD FOR CONVERTING SOLID FERROUS METAL TO STEEL

Inventors: Richard W. Hyde; Herman P. Meissner; Charles L. Kusik, all of Winchester, Mass.

Assignee: Columbia Gas System Service Corporation, New York, N.Y.

Filed: Nov. 23, 1971

Appl. No.: 201,382

ABSTRACT

This invention relates to a method for converting solid ferrous metal to steel which comprises:

a. providing a molten pool of ferrous metal containing less than about 1 percent carbon by weight;

b. introducing a charge of solid ferrous metal containing an average of less than about 1 percent carbon by weight into said molten pool;

c. introducing into said molten pool an amount of oxygen-rich oxidant and a fuel in a ratio such that an exothermic reaction which is substantially neutral or only mildly reducing to iron oxide occurs predominantly below the surface of the molten pool releasing sufficient chemical enthalpy of reaction to melt the feed ferrous metal;

d. recarbonizing the molten ferrous metal with an amount of carbon which is sufficient to impart a carbon content to the melt to produce steel;

e. withdrawing all or a portion of the molten steel.

24 Claims, 6 Drawing Figures
3,772,000

METHOD FOR CONVERTING SOLID FERROUS METAL TO STEEL

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of our earlier filed application Ser. No. 739,826, filed June 25, 1968, now abandoned.

BACKGROUND OF THE INVENTION

Field of the Invention

The instant invention relates to the conversion of ferrous metal to steel and specifically, to a method for converting solid ferrous metal to steel which comprises adding to a molten pool of ferrous metal a solid charge of ferrous metal containing an average of less than about 1 percent carbon by weight, introducing into the molten pool an oxygen rich oxidant and a fuel in a ratio such that an exothermic reaction which is substantially neutral or only mildly reducing to iron oxide occurs predominantly below the surface of the molten pool releasing sufficient chemical enthalpy of reaction to melt the feed ferrous metal, recarbonizing the molten ferrous metal with an amount of carbon which is sufficient to impart a carbon content to the metal to produce steel and withdrawing all or a portion of the molten steel.

Description of the Prior Art

Increasing quantities of ferrous scrap are becoming available for conversion to steel and the quantities actually used are not keeping pace with the quantities available. This is in large part due to the growth in oxygen steelmaking via the Basic Oxygen Process (BOP) and oxygen lancing in the open hearths. The basic reason for this is that the use of oxygen in both the open hearth and the basic oxygen furnace has significantly reduced the time of producing heats of steel. Those processes rely on the oxidation of dissolved impurities such as carbon, silicon, manganese, etc., in the blast furnace hot metal to generate the necessary heat. As a result, they have placed additional emphasis on hot metal and blast furnace production and have deemphasized the use of scrap which is generally relatively low in these oxidizable impurities. This is particularly true of the Basic Oxygen Process where the ratio of molten pig iron to cold scrap typically ranges between 75 to 25 or 70 to 30. This has meant that such steel plants consume their internally generated scrap but consume little additional outside scrap.

Several processes using oxygen containing gases in direct contact with the molten iron have been operated. The earliest were the Bessemer and Thomas converters using air as the source of oxidant. However, due to the nitrogen embrittlement of the resulting steel, the Bessemer and Thomas converter processes have declined in importance in modern steel-making practice. Bottom or side blowing with pure oxygen in a Bessemer or Thomas converter has not been practical because of excessive temperatures around the points of oxygen entry. The development of the (BOP) or (LD Process) provided a successful technique for introducing pure oxygen by lancing directly onto the surface of molten pool of iron, thus eliminating excessive refractory wear experienced with bottom blown converters with oxygen or highly enriched air. (See, for example, U.S. Pat. No. 2,800,631.) In a similar method pure oxygen is now commonly introduced into open hearths by lancing onto the bath from above, and oxygen-enriched air is used in the end burners as a means for obtaining higher flame temperatures and increasing the heat transfer to the steel bath. This also has resulted in a decrease in heat time in the open hearth but does not provide for increased use of scrap over former open hearth practice, which typically was 50 percent scrap and 50 percent metal charges.

It would, however, be desirable to be able to make steel from scrap by an economically feasible method, thus drawing on this large, only partially consumed supply of metallic iron. Several such methods have been proposed. One of these methods is a modified converter process called the Kaldo oxygen steel-making process which has the advantage of being operated with 50 percent scrap and 50 percent hot metal. However, this process has certain disadvantages, one of which is a high consumption of refractories in the rotating vessel in which the process is carried out. Another proposed method for achieving higher scrap utilization in the basic oxygen furnace involves the addition of relatively expensive additive fuels such as calcium carbide, ferro silicon, silicon carbide, etc. However because of the high cost of these additives, this modification of the (BOP) process is not widely used.

Another method for obtaining high ratios of scrap to hot metal is the so-called "dual hearth" process which divides the hearth of the open hearth into two sections. The sections are fired alternately; while a hearth of steel is being refined in one section, the hot off-gases pass over the scrap in the other section, melting it down and preparing it for hot metal addition and refining. The purpose of this method is to increase the use of scrap in the open hearth without having to employ the longer heating periods typically involved in normal open hearth practice using charges of 50 percent hot metal and 50 percent scrap.

Attempts have also been made to develop a steel-making process based upon the preheating and melting of scrap in the shaft furnaces or cupolas. While steel scrap can be preheated in shaft furnaces or similar devices, oxidation can occur simultaneously with this preheating and becomes very rapid near the melting point. This requires the use of gases which are strongly reducing. Because of this problem of oxidation, along with bridging and blockage in the shaft, it is usually necessary to add either coke or pig iron as part of the cupola charge, resulting in a metal which is high in carbon and which therefore must be subsequently refined in a steel-making furnace converter.

None of the above-described methods for using scrap is being widely used, for each has one or more major disadvantages associated with it. The accepted process for producing steel from scrap in wide use today is the traditional electric arc furnace process. While the electric arc furnace process is ideal for producing alloy and high quality steels, it can be relatively expensive for the production of carbon steels. Furthermore, the cost of power and of electrodes may be too high to justify the adoption in small or intermediate sized steel-making operations. Moreover, the nature of the power demands of the electric arc process is such that it is not always possible to install electric arc furnaces on power distribution systems. An electric arc furnace is not a desirable power consumer on a grid system unless the system is very large because of the widely fluctuating char-
acteristics of the furnace operation. Otherwise, it is necessary to install power generating equipment specifically for the electric arc furnace.

It becomes apparent then that there exists a real need for an improved method and apparatus for converting ferrous scrap steel to steel or other usable forms. The use of ferrous scrap steel either alone or with a minor amount of pig iron offers a potentially valuable source of iron values for steelmaking.

**SUMMARY OF THE INVENTION**

The process of this invention provides an improved method for converting ferrous metal particularly in the form of scrap iron or scrap steel containing an average of less than about 1 percent carbon into a usable steel of desired carbon content. The process of this invention possesses the considerable advantage over other fuel-fired processes in being able to utilize a 100 percent solid charge. The process is inexpensive, rapid, and exhibits a flexibility of operation which permits varying and accurate control of the resulting steel composition and hence the properties of the resulting steel.

The invention can advantageously be used in conjunction with a pneumatic steel-making process in an integrated steel plant which is not limited to the ratio of scrap iron or steel to pig iron in the ferrous charge. The steel-making process of this invention is also particularly well suited for use in small nonintegrated plants for producing low and medium carbon steels from scrap.

Broadly stated, this invention relates to a method for converting solid ferrous metal to steel which comprises:

a. providing a molten pool of ferrous metal;

b. introducing a charge of solid ferrous metal containing an average of less than about 1 percent carbon by weight into said molten pool;

c. introducing into said molten pool an amount of oxygen-rich oxidant and fuel in a ratio such that an exothermic reaction which is substantially neutral or only mildly reducing to iron oxide occurs predominantly below the surface of the molten pool releasing sufficient chemical enthalpy of reaction to melt the feed ferrous metal;

d. re-carbonizing the molten ferrous metal with an amount of carbon which is sufficient to impart a carbon content to the metal to produce steel; and

e. withdrawing all or a portion of the molten steel.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a longitudinal cross-section of a furnace suitable for carrying out the method of this invention in which oxygen is introduced into the metal from the surface and fuel is introduced underneath the melt;

FIG. 2 is a diagrammatic representation of a complete system including auxiliary components for controlling the flow of the various fluids;

FIG. 3 is a longitudinal cross-section of another embodiment of a furnace for carrying out the method of this invention in which both oxygen and fuel are introduced beneath the melt;

FIG. 4 is a cross-section of the bottom section of the furnace of FIG. 3 taken along line 4—4 of FIG. 3;

FIG. 5 is a longitudinal cross-section of yet another embodiment of a furnace for carrying out the method of this invention in which both oxygen and fuel are introduced at the surface of the melt; and

FIG. 6 is a cross-section of the central portion of the furnace of FIG. 5 taken along line 6—6 of FIG. 5.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

FIG. 1 represents one embodiment of the apparatus of this invention and this figure will be used subsequently to describe the method of this invention. In FIG. 1 a furnace suitable for carrying out the process of the invention is generally indicated by the numeral 10. It will be seen to have a vertical wall 11 which is protected by a suitable refractory liner 12. The furnace wall also has a bulged portion 13 lined with refractory 14. The bulge defines within the furnace housing a depression 15 which has a volume such that when the furnace is rotated through about 90° in the direction of the arrow, the depression will be capable of containing the amount of molten material present in the furnace at start-up. The furnace has a cover member 18 with a refractory lining 19 and a bottom member 20 lined with refractories 21. In the bottom of the furnace are a number of tuyeres 23 which provide fluid communication between the furnace and a removable fuel inlet system. The tuyeres are of conventional construction such as those commonly used in Bessemer converter operations and therefore need not be described further. This fuel inlet system is made up of a housing 24 which defines a plenum chamber 25 which in turn is in fluid communication with a fuel source through an inlet conduit 26.

Within the furnace volume 29 is the molten metal 30 shown to have scrap 31 suspended therein and to have a layer of molten slag 32 on the surface thereof. It is understood that this molten slag layer is probably mixed with the bulk metal bath during the processing by the turbulence in the bath caused by the high velocity input of the oxidant, the velocity input of the fuel and the exothermic reaction taking place therein, causing splashing of the slag; and some of the molten metal within volume 29. The intimate contact of the slag with the molten metal provides an effective means for slag refining of the scrap, for it makes it possible to remove oxidized impurities (e.g., silica, manganese and refractory metals, etc.) from the melt into the slag. The furnace may be constructed so as to make it possible to pressurize volume 29 to reduce violent boiling or agitation in the melt when this is desirable.

In the modification shown in FIG. 1 high purity oxygen or other oxidant is introduced through the top of the vessel where it immediately dissolves in the molten ferrous metal or reacts with dissolved impurities or iron producing heat and oxides which in turn are suspended or dissolved in the molten metal or slag. This can be accomplished by introducing the oxygen through oxygen lances 34 and 35 in accordance with the well-known procedure now used in the basic oxygen furnace. These lances are normally water cooled; and inasmuch as they are of a well-known design, the lances need not be described further. The fuel is introduced into the melt by way of the tuyeres underneath the melt. The fuel reacts with the dissolved oxygen also producing heat release for scrap melting. Iron oxide contained in the melt is reduced by the fuel gases to molten iron. The overall or net reaction occurring in the melt is the partial oxidation of the fuel with oxygen. If more oxygen is introduced than can react with the fuel, a net production of iron oxide will result. This excess iron oxide can be
chemically reduced to iron by decreasing the oxygen flow rate or otherwise altering the oxygen-fuel ratio to cause the iron oxide to be chemically reduced to iron.

A gas outlet 37 is provided for removing the off-gases from the furnace. The furnace of FIG. 1 is adaptable for batch or “continuous” operation. If it is to be used for continuous operation, a scrap inlet such as chute 38 will be provided at the top and a valve-controlled tapping conduit 39 near the bottom level of the melt, the conduit 39 being adapted for withdrawing molten metal. Finally, in keeping with normal Bessemer furnace design, there is shown in FIG. 1 a trunnion 40 which is adapted to rotate within suitable pinion and supports in accordance with normal practice.

Before describing the method in detail, it will be helpful to examine FIG. 2 which is a somewhat diagrammatic representation of a typical overall system involving the furnace and using the method of this invention. The furnace again is shown by the general number 10 and in FIG. 2 like numbers refer to like elements in FIG. 1. It will be seen that the trunnion 40 is held in a suitable trunnion support and bearing housing 41 having supports 42 and a foundation 43.

Inasmuch as the off-gases can advantageously be used in various ways to replace at least as well as the oxygen and the fuel, it will be convenient to begin the description of FIG. 2 with means for the disposition of these off-gases. In FIG. 2 an off-gas line 51, controlled by valve 52, is seen to communicate with a combustion chamber or heat exchanger 53 which could be adapted for burning the high temperature off-gases (which contain a considerable amount of hydrogen and carbon monoxide) with air which is introduced into combustion chamber 53 through line 54 controlled by valve 55. Alternatively the hot off-gases (containing much sensible heat) could directly contact and preheat scrap. The burned off-gases may then be discharged directly through discharge line 56 controlled by valve 57. Alternatively, the unburned off-gases may be transferred by line 58, controlled by valve 59, into a suitable conduit 60 which communicates with a condenser-scrubber 62.

Combustion chamber-heat exchanger 53 is preferably constructed to consist of a series of stacked combustion chambers, each receiving a limited amount of air or other oxidant. The scrap is fed so that it passes downwardly through the succeeding combustion chambers while the off-gases are passed upwardly and burned. This results in the achievement of favorable gradients in both temperature and combustion gas composition, for the hottest scrap is exposed to those combustion gases which are the most reducing in nature, that is, those coming from the furnace; while the cold scrap entering the combustion chamber-heat exchanger is exposed to the oxidized off-gases. This type of scrap preheating eliminates or minimizes the oxidation of the scrap which is undesirable.

It will also be seen in FIG. 2 that the off-gases from the furnace 10 may be transferred directly by means of line 51 into line 60 (through valve 61) if it is desired not to perform any combustion of these gases at this point. The choice will depend on whether or not it is desirable to directly preheat the scrap, as will be described subsequently.

The off-gases after passing through the condenser-scrubber 62 may be directly discharged through line 63, or by proper operation of valves 64 and 65, they may be directed into one or two alternative paths. The first of these paths is by way of conduit 66, controlled by valve 67, which leads to the main fuel source line so that the unburned off-gases may be recycled in the furnace. The other alternative at this point is to close valves 65 and 67, open valve 64 and permit the gases to enter a combustion chamber 69 which is adapted for burning the gases with air introduced through line 70 controlled by valve 71. The combustion gases from combustion chamber 69 may then be introduced by way of conduit 72 into an indirect heat exchanger 73 for subsequent discharge through line 74 and likewise by way of a branch conduit 75, controlled by valve 76, into an indirect heat exchanger 77 for discharge by line 78. The purpose of heat exchangers 73 and 77 is to furnish heat for preheating the fuel and oxygen prior to the introduction of these reactants components into the furnace 10.

Oxygen is supplied from a suitable source 80 which is shown in FIG. 2 to be high-pressure oxygen. It is of course within the scope of this invention to use low pressure gaseous oxygen, liquid oxygen and any suitable means for vaporizing it prior to its introduction into the oxygen line 81. The oxygen line 81 passes through the heat exchanger 7 and is connected to lance 34 which extends into the furnace.

The fuel source 90, which may be any source of a suitable fuel, is connected by conduit 91, controlled by valve 92, to the fuel inlet line 26. The conduit 91 passes through the indirect heat exchanger 73 for preheating the fuel. If combusted off-gases are to be recirculated through the furnace, they are conveniently introduced into fuel line 91. The fuel may also be introduced above the surface of the melt within the furnace and this may be done by way of fuel line 91 and 93, controlled by valve 94, which passes through the indirect heat exchanger 73 prior to its communication with the upper portion of the furnace. It is within the scope of this invention to use a fuel which is mixed with some air or oxygen and so there is furnished an auxiliary oxygen source 82 which by line 83 and valve 84 is connected to fuel line 91. This oxygen or oxygen-containing gas may also of course be supplied by the source 80. It is also within the scope of this invention that heat exchanger 53 could be so designed as to permit preheating of scrap directly as described above and preheating of fuel and oxygen indirectly through separate heat exchangers in contact with the off gases from the direct scrap preheating.

Finally, the arrangement of FIG. 2 is adapted for preheating the scrap which is to be introduced into the furnace. This is done by passing scrap through the preheating chamber 53 before introducing it by suitable means, represented diagrammatically in FIG. 2 as conduit 96, into the furnace.

The arrangement of FIG. 2 is such that it is not necessary to choose alternates in all cases, but it is possible to use a combination of the preheating systems. For example, a portion of the off-gases may be introduced into combustion chamber 53 while the remaining portion is introduced in the combustion chamber 69. This in turn would provide means for preheating both the scrap as well as the fuel and the oxygen. It is of course within the scope of this invention to introduce the fuel only beneath the surface of the melt or beneath the surface as well as at the surface and to vary the fluid flow in the system of FIG. 2 in any desired fashion.
The operation of the furnace of FIGS. 1 and 2 may now be described and the method of this invention detailed with references to these figures.

The process is operated starting with a hopper of molten steel from the previous heat sufficient in volume to accommodate the solid ferrous metal additions. While maximum scrap to steel ratios have not been experimentally determined, it is felt that a ratio of 1:1 is appropriate (i.e., about one-half ton ferrous metal charge to one-half ton molten metal). The ferrous metal charge can consist of scrap steel, scrap iron, pre-reduced pellets, or other suitable source. While the ferrous scrap is being added, the furnace is tilted about 90° from the position shown in FIG. 1 to provide sufficient volume for this metal hopper so that the molten metal is out of contact with the tuyere openings. The initial solid scrap charge (either preheated or cold) is preferably made to the vessel in this tilted position, at which time gaseous fuel is blown by way of fuel line 26, plenum chamber 25 and tuyeres 23 into the furnace. The furnace is then tilted to its upright position and the oxygen lance 34 (and 35 if used) lowered to commence the oxygen blow. Although FIG. 1 shows two oxygen lances, only one may be used as shown in FIG. 2. Gas must be continuously introduced into the furnace throughout this start-up period and all the time when the vessel is in its upright position, or at any time that the tuyeres are covered or partially covered with molten metal. The gas pressure and flow rates must be such as to prevent any melt from passing through or clogging the tuyeres.

The addition of scrap to the furnace may be made in one initial batch or in several batches during the course of the heat, depending on the gross bulk density of the scrap. The higher the bulk density of the scrap used, the fewer the charges may be. With light scrap more than one charge may be required. If the ratio of molten steel from the previous heat to new scrap charge is high, then the scrap may be charged in one or two batches. On the other hand, if the ratio of steel to new scrap is low, a greater net production of new steel per heat will result but more numerous scrap additions must be made. It is advantageous for the scrap to be largely submerged in the molten steel and that the continuous phase in the bath be molten steel or iron at all times.

All of the reactions which occur within or below the surface of the melt are not known. The types of reactions which will occur will vary and depend upon numerous factors including the type of oxidant used, the particular fuel employed, the oxidant-fuel ratio used, the impurity content of the ferrous metal being teared, the type and amount of any materials which may be added to the melt during processing, the processing conditions, the properties of the end product desired, and so forth. Some of the reactions which occur when using relatively pure oxygen and methane as a fuel are described below.

At the start of the gaseous fuel flow using natural gas, the overall effect is endothermic adjacent the refractory lining at the area of hydrocarbon fuel addition, i.e., if hydrocarbons, especially methane, are used, the melt is chilled by the sensible heat needs and the endothermic cracking reaction (1).

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]  
(1)

However, oxygen lancing should be started as soon as possible in order to take advantage of the overall exothermic reaction of oxygen with the fuel. Since the melting point of steel scrap is in the vicinity of 2750°F., the operations of the vessel must be at relatively high temperatures, e.g., in the range of 2900°F.-3000°F.

The heat generation is the result of the oxygen reacting with the iron, its oxidizable impurities, e.g., C, S, Mn, etc., and the fuel gases such as hydrogen and carbon monoxide.

In order to obtain the required heat in the bath, it is desirable to operate the molten pool at relatively high oxygen levels which is consistent with low carbon levels. This promotes the oxidation of hydrogen. On the other hand, if the melt is operated at high carbon levels, the environment is more reducing and the hydrogen and the carbon monoxide rising through the melt are oxidized to a lesser extent. Even if the carbon levels are high in the molten steel, there will be substantial amounts of iron oxide (FeO) in the refining slag layer. This means that the hydrogen and carbon monoxide passing up through the bath may be oxidized as a result of the reaction with the FeO in the slag according to equation (2).

\[ \text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \]  
(2)

At the temperatures involved (about 3000°F.) this reaction is very slightly endothermic. The same is true of reaction (3) between carbon monoxide and iron oxide.

\[ \text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \]  
(3)

However, the overall reaction involves the combination of carbon with oxygen and the summation of the oxidation of the iron and its contained impurities plus the decomposition and reduction reactions (1), (2), and (3).

The overall reaction is exothermic.

Because the endothermic nature of reaction (1) brings about a chilling effect at the bottom tuyeres and hence presents the problem of potential tuyere plugging, it may be advantageous to introduce a mixture of oxygen (from an auxiliary source such as 82 of FIG. 2) and hydrocarbon fuel, e.g., methane and oxygen through fuel line 26 beneath the surface of melt 30. Such a mixture should of course contain a quantity of oxygen which is below the spontaneous combustion limits of the mixture at the temperatures and pressures involved. As previously mentioned, oxygen lancing from above the melt surface should be started as soon as possible in a manner similar to that employed in the present Basic Oxygen Process. As in the case of the Basic Oxygen Process, heat is generated; but the similarly stops since in this process the hydrocarbon fuel, e.g., natural gas is oxidized to CO, CO₂ and water vapor in accordance with the following overall reaction (4).

\[ \text{CH}_4 + 0.5 \cdot (1+x+y) \cdot \text{O}_2 \rightarrow y\text{H}_2\text{O} + (0.5n-y)\text{H}_2 + (1-x)\text{CO} + x\text{CO}_2 \]  
(4)

The y moles of water vapor and the x moles of carbon dioxide formed when the off-gases are at the thermodynamic equilibrium with the dissolved oxygen in the steel melt may be determined in the usual way from the
free energies of reaction at the temperatures of the melt. For the oxides of carbon and hydrogen, these relationships and equilibrium constants are:

\[
\begin{align*}
\text{CO} + \text{O} & \rightarrow \text{CO}_2; \quad K_1 = \frac{\text{PCO}_2}{[\text{PCO}]} = \frac{[a_o]}{[a_o] (1-x)} \quad (5a) \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 + \text{O} & \rightarrow \text{H}_2\text{O}; \quad K_2 = \frac{\text{PH}_2\text{O}}{[\text{PH}_2]} = \frac{[y]}{[a_o] (1-y)} \quad (5b) \\
\end{align*}
\]

wherein \(a_o\) is the oxygen activity in the molten metal. It will be seen that the pressure, \(\pi\), has no influence on the ratio of \(\text{CO}_2\) to \(\text{CO}\) or of \(\text{H}_2\text{O}\) to \(\text{H}_2\).

The heat generated by the overall exothermic reactions serves to melt the scrap by liquid convection heat transfer from the molten steel to the solid scrap.

In steel production at temperatures in the range of 2-900\(^\circ\)F to 3100\(^\circ\)F, the \(\text{CO}_2/\text{CO}\) ratio must be low to satisfy the equilibrium of reactions (5a) and (5b). On the other hand, the reverse is true at these temperatures with respect to the ratio of \(\text{H}_2\text{O}/\text{H}_2\) in that it is relatively high, i.e., 0.75. This means that a substantial proportion (over 45 percent) of the hydrogen from reaction (1) is oxidized with a very significant heat release. This is consistent with the experience on the process of this invention.

The process is continued with subsequent additions of scrap. Each time scrap is added, the oxygen lance is lifted and the scrap charge added with fuel being introduced at a reduced rate through tuyeres. Refining of the melted scrap proceeds simultaneously with the oxidation of such impurities of alloying elements in the scrap of silicon, manganese, vanadium, columbium, zinc, titanium, aluminum, etc.

The process of this invention utilizes solid ferrous metal charges containing on an average of less than about 1.0 percent carbon by weight. The process will not operate properly at steady states with charges containing significantly greater quantities of carbon. Generally, the charge will consist of scrap steel or iron containing about 0.1 percent carbon and usually not less than 0.04 percent carbon by weight. The higher the oxygen content of the steel (and thus also the carbon content), the greater is the utilization (oxidation) of the hydrogen, and the heat release, and the lower is the hydrogen content of the steel at the completion of the heat. The carbon content of the heat can of course be somewhat controlled by adjusting the ratio of oxygen to fuel. As the fuel-oxygen ratio increases, the carbon content of the heat increases and vice-versa. Carbon content can also be increased by blowing fine solid carbon or carbon containing solid in suspension in the hydrocarbon fuel, or by using hydrocarbon fuels which have relatively high C/H ratios. By proper adjustment of fuel composition and oxygen feed, a portion of the carbon may be furnished directly from fuel cracking according to Equation (1).

Each time the lance is removed for scrap addition, the oxygen level tends to decrease and the carbon content to increase. However, it is generally preferred to operate with low carbon levels in the melt, i.e., near oxygen saturation, because this promotes more extensive oxidation of the hydrogen. For simple equilibrium considerations, general Equation (6) may be written using methane as a fuel and assuming a melt saturated with oxygen (in equilibrium with the reduction of \(\text{FeO}\) to \(\text{Fe}\)).

\[
\text{CH}_4 + 0.9950\text{O}_2 \rightarrow 0.85\text{CO} + 0.15\text{CO}_2 + 0.84\text{H}_2\text{O} + 1.1\text{H}_2 \\
\]

(6)

Such conditions promote the most extensive oxidation of the hydrogen in the steel bath. However, it is not necessary that the bath be at complete oxygen saturation since at or near the lance there are transient, nonequilibrium conditions where the oxygen content is much higher and where oxidation of hydrogen and carbon monoxide is carried to the extent indicated by reaction (6) even though the average oxygen content of the melt may not be at saturation. Thus it is preferred to operate at low carbon levels (under 10 points), with adjustment of carbon at the end of the heat to the desired level. If higher carbon levels are required by the heat specifications, carbon content may be easily increased by increasing the fuel/oxygen feed ratio by introducing solid carbon or higher hydrocarbon fuels suspended in the fuel gas or by subsequent ladle additions. During the period at the end of the heat when carbon build-up is required, it is possible to stop oxygen lancing while continuing the fuel blowing to promote carbon addition. This latter practice, however, tends to chill the melt. One way to minimize this chilling effect is to surface blow the vessel during fuel addition with oxygen to oxidize the off-gases in the carbon monoxide to carbon dioxide and the hydrogen to water vapor, reactions which will impart radiant heat to the bath. Another way to minimize the chilling effect is to inject solid carbon suspended in the gaseous fuel injected beneath the melt. This reduces the chilling effect per part of carbon addition because the endothermic nature of the dissolution reaction for solid carbon is far less than the endothermic cracking reaction for hydrocarbons, especially for methane.

Recarbonization of the melt to form steel having a carbon content of up to about 0.1 percent is conveniently accomplished by utilizing the carbon content in hydrocarbon fuel. For steels requiring a higher carbon content, it is more advantageous to add additional carbon directly to the melt.

Recarbonizing at the end of the heat with hydrocarbon fuel will impart dissolved hydrogen to the steel which is undesirable particularly in fully and semi-killed steels. Hydrogen can be removed by vacuum degassing, but this involves a second operation. Hydrogen can also be removed rather easily by jet degassing which usually involves bubbling an inert gas through molten steel. In the process of this invention, however, the preferred method for removing hydrogen is by injecting carbon dioxide into the bottom tuyeres at the very end of the heat just prior to pouring. Carbon dioxide will react with the hydrogen in accordance with the following reaction:
Hydrogen removal is rapid because the resulting carbon monoxide will tend to strip hydrogen as is the case with jet degassing.

Finally, it will usually be desirable to excise some control over the sulfur content of the resulting steel. This is most readily accomplished by minimizing the sulfur introduced with the fuel. It is a relatively easy matter to desulfurize any gaseous hydrocarbon fuel used. This is in direct contrast to the difficulties experienced in desulfurizing coal, coke and liquid fuels.

When it is desirable or necessary to remove substantially all or a portion of sulfur which may have been contained in the ferrous metal charge, slag forming components such as lime and silica in a weight ratio of 3:1 can be added to the melt so form a complete with the sulfur. In such a case, the oxygen to fuel ratio should be reduced upon addition of the slag forming substance to a level whereby the reaction of oxygen and fuel will remain exothermic but the formation of iron oxide which is soluble in slag will be substantially decreased. This reduction in oxygen activity should be maintained throughout the entire period of slag formation and upon decantation of the slag, the previous oxygen to fuel ratio should be restored in order to compensate for the cooling effect brought about by removal of the slag from the melt. When using natural gas or methane as a fuel, it is desirable to maintain a molar ratio of oxygen to fuel of about 0.5:1.

FIGS. 3 and 4 illustrate an embodiment of this invention in which both the fuel and the oxygen are introduced beneath the melt 30 for the furnace. In this figure like numbers refer to like elements in FIGS. 1 and 2. In order to introduce both of the reaction components beneath the melt, it is desirable to modify somewhat the bottom portion of the furnace. Thus the bottom 100 in FIG. 3 defines a fuel plenum chamber 101 and a chamber 102 for oxygen-containing gases which are divide by a suitable divider such as 103. A fuel line 105 provides the required communication between a fuel source (not shown) and the fuel plenum chamber 101; and an oxygen line 106 provides the required communication between an oxygen source (not shown) and the oxygen plenum chamber 102. Because intensive heat may be generated at the outlet of those tuyeres from which oxygen is introduced into the melt, it may be necessary to mix some diluent with the oxygen. Thus there is provided line 107 which communicates with oxygen line 106 and is adapted to carry a suitable diluent. The diluent may be either an inert gas or largely oxidized off-gases from line 66 (FIG. 2). Control of temperature at the outlet of the tuyeres is necessary to prevent excessive refractory wear in this vicinity. The furnace of FIG. 3 has a gas-withdrawal line 111.

In the operation of the furnace of FIG. 3, the chemistry is essentially that which has been described in detail above for the operation of FIG. 2, the only difference being that the fuel and oxygen are both introduced beneath the bottom of the melt 30.

The furnace embodiment shown in FIGS. 5 and 6 illustrates a modification of the apparatus and the method. In this modification both the oxygen-containing gases and the fuel, whether liquid or gas-
to accomplish the objects of this invention and the diluents do not adversely affect the operation of the process according to this invention or the resulting steel. For example, the oxidant source can include not only pure oxygen but also relatively pure oxygen such as oxygen-enriched air and carbon dioxide. The amount of air employed should be held down to a concentration where the nitrogen content therein will not adversely affect the nitrogen content of the resulting steel desired.

The ratio of the oxidant to the fuel will vary depending upon the kind of oxidant and fuel employed, as well as the solid fuel impurity content of the ferrous metal being treated, the type and amount of any materials which may be added to the melt during the processing, and so forth. For example, if the ferrous metal being treated contains approximately 1 percent carbon, it will not be necessary to use as much fuel as it would if the ferrous metal being treated contained only 0.5 percent carbon. The ratio of the fuel to the oxygen should advantageously produce a neutral or reducing environment within the melt. The term "mildly reducing" refers to that degree of reducing just below the point at which iron oxide is formed when no slag is present.

If the oxygen is in excess, iron oxide will be formed. Although this may not be particularly undesirable, it will require an increase in the fuel or a decrease in the oxygen in order to chemically reduce the iron oxide. An oxidizing environment over prolonged periods must be avoided since substantial quantities of iron oxide would result. The problems involved in using an excess of fuel will vary depending upon the fuel used. An excess of methane, for example, which produces an endothermic reaction, might cause a reduction of the melt temperature or simply result in a waste of the fuel since it will not be consumed during the reaction and will be combined with the off-gases, will not be consumed during the reaction and will be combined with the off-gases.

When using natural gas or methane as a fuel, it is desirable to maintain a molar ratio of hydrocarbons to oxygen of about 1:1. The particular ratios of natural gas or other fuels to the oxygen will vary depending on the fuel employed and other factors discussed above and can be determined by routine testing and calculations by those skilled in the art.

If the ferrous metal contains a significant amount of impurities which act as a fuel for generating heat by reaction with an oxidant, these will be consumed during the processing, and it may be necessary or desirable during some later stage of processing of the ferrous metal to increase the amount of fuel to maintain a neutral or reducing environment to prevent undue oxidation of the iron.

Although the process of this invention has been described above using essentially all scrap steel or scrap ferrous metals where it is most advantageous, the ferrous metals or scrap steel which can be utilized according to this invention are those ferrous metals or mixtures thereof containing insufficient fuel impurities such as carbon, silicon, manganese, and so forth, to generate the necessary heat for converting or refining the ferrous metal into a usable steel product by use of oxygen alone. For example, conventional hot metal pig iron would be excluded from these terms since it contains sufficient fuel impurities to react with the oxygen in the Basic Oxygen Process, and thus the use of an additional fuel would not be necessary or required. The terms "ferrous metal" and "scrap steel" do, however, include both iron and steel from known scrap sources such as auto bodies, internally generated scrap as is well known in the art, as well as mixtures of pig iron and ferrous metal, such as scrap steel having a combined solid fuel impurity content sufficiently low so that the necessary heat cannot be generated solely by oxygen lacing by the Basic Oxygen Process.

The invention also contemplates the addition of various and known refining chemicals such as calcium oxide, ferrosilicon, and the like, to the melt. This may be done by adding such materials along with the scrap or suspending them in either the oxygen or fuel streams.

It will be seen that this invention provides a process and apparatus for converting solid ferrous metal scrap to usable steel without encountering the disadvantages associated with the prior art methods and apparatus described. Since the reactants (oxygen and fuel) can be provided in almost any geographic location, the application of the process is not limited to a few special areas such as in the electric arc method. Finally, the ability to control the chemical make-up of the reactants makes it possible to control the composition of the steel.

The oxidant or relatively pure oxygen when introduced into the melt is dissolved or absorbed, basically saturating the molten bath with oxygen, permitting the exothermic reactions to occur below the surface of the melt and causing the heat to be released from the reaction below the surface of the melt. The reaction occurring below the surface of the melt is believed to cause a circulation or a fairly violent agitation within the melt and is fairly evenly distributed throughout the melt, eliminating any hot spots.

The molten baths 30 and the slag layers 32 shown in the drawings are shown in the quiescent state. The slag layer is probably intermixed with the molten ferrous metal bath during processing due to the agitation. Whether the entire bath is in agitation during the processing and the slag layer intermixed therewith is not known.

The amount as well as the pressure of the oxygen input can be varied quite widely according to this invention and will depend upon a number of variables such as the type of vessel being employed, the amount and type of ferrous metal charge being treated, and so forth. The amount of oxygen will of course have to be correlated with the amount of reductant fuel being introduced in the molten pool as previously discussed. The rate or velocity of the oxygen input can also be varied, but it should be sufficient to insure substantially complete dissolving of the oxygen in the molten pool so that the desired reaction between the oxygen and the reductant fuel can take place within or beneath the surface of the molten pool.

Oxygen pressures can range, for example, between 50 to 150 pounds, but the invention is not limited to this particular pressure range. Typically the oxygen cannot impart sufficient energy to the molten pool to stir or agitate it by itself. The exothermic reaction occurring within the pool may also cause agitation of the molten pool by thermal currents. However, the main agitation of the melt is undoubtedly caused by the gas being blown up through the melt. The exothermic reaction also has the advantage of being able to maintain the melt temperature, allow further time for the ad-
tion of various additives such as carbon to form the steel desired, and no prevent oxidation of the iron even when extremely low carbon or impurity content is contained in the molten pool.

The lances and tuyeres that can be used according to this invention can be readily designed by those skilled in the art, with respect to opening sizes, for example, taking into account the type of the charges to be treated, the velocity and volume of gases required or desired for the particular charge, and so forth.

EXAMPLE I

400 pounds of cold scrap steel containing approximately 0.2 percent carbon were charged into a 16-inch internal diameter furnace having maximum capacity of 1000 pounds. The furnace was equipped with induction heating coils and the cold scrap steel melted by induction heating.

Natural gas as commercially available was then introduced into the melt through four 1/4-inch diameter tuyeres which communicated with the bottom wall of the furnace as shown in FIG. 1. The gaseous oxygen was simultaneously lanced onto the surface of the molten steel through a single 1/4-inch diameter lance of conventional design.

The flow rates of the natural gas and the oxygen were maintained essentially equal, starting out at about 10 standard cubic feet per minute and gradually increasing the flow rates to about 35 standard cubic feet per minute. The oxygen flow rates were increased by increasing the back pressure from about 50 to 130 pounds.

As the flow rates of both the oxygen and natural gas were increased, less heat was required from the induction coils. When the higher flow rates were reached, the reaction between the oxygen and natural gas was sufficient to maintain the steel in the molten condition as well as to overcome substantially all of the heat losses, which we relatively high for the small vessel being used. The oxygen and natural gas input was stopped, the vessel tilted, and approximately 100 pounds of the molten steel were poured into molds without the addition of carbon or other additives. The resulting steel contained approximately 0.01 percent carbon. The carbon content of the resulting steel could of course be modified to the extent desired as described herein by blowing carbon into the bath through a steel pipe or by adding it to a holding ladle or by any other conventional means.

The vessel was then tilted to the upright position, and approximately 20 pounds of additional scrap steel containing about 0.2 percent carbon were added thereto, the top of the vessel was closed again, and the introduction of the natural gas and oxygen restarted and continued until the additional charge was melted.

The process of heating, pouring and adding additional scrap as described above can be continued.

Various changes in the method and apparatus can of course be made by those skilled in the art to carry out the above-described process without parting from the scope of this invention. For example, as previously pointed out, the tuyeres 23 in FIG. 1 could be closed off or eliminated and either one of the lances 34 or 35 lowered into the bath to cause the exothermic reactions to occur substantially completely below the surface of the bath. It is thus intended that all matters contained in the above descriptions and shown in the accompany-

EXAMPLE II

Operation I. Initial Oxidation

By assuming a 50 percent heel and 50 percent scrap addition, 1040 lbs. of heel will contain about 0.10 percent (1 lb.) of carbon. On combustion to CO it releases heat to one ton of metal. Melt oxygen activity will be 0.95 at the end of this operation.

Operation 2. Meltdown

Subsequent to the oxidation of the heel and while maintaining an oxygen activity of 0.95, scrap and 4.16 lbs CaO will be melted and the silicon in the scrap will be oxidized. Some iron will be oxidized and appear temporarily in the meltdown slag.

Operation 3. Superheat

After completion of meltdown, the melt is superheated to 3060° in order to prepare for deoxidation. This operation is carried out with an oxygen activity of 0.95.

Operation 4. Deoxidation

At this point in time, one starts deoxidizing the melt which is accompanied by FeO reduction from the slag. To reduce FeO from the slag will require about 32,000 to 43,000 Btu per mole of FeO reduced. This comes to an average of about 37,800 Btu/mole.

After this initial bath deoxidation, the melt oxygen activity is reduced to about 0.83, whereupon flux additions are made to make a final slag.

Operation 5. Final Slag and Desulfurization

While CaO and SiO₂ are added for desulfurization, oxygen activity is reduced from 0.83 to 0.50. No significant amount of FeO is reduced or oxidized. Calculations indicate that about 166 lbs. of slag will be required to reduce sulfur in the scrap from 0.04 to 0.025 percent. Since the heel contains 0.025 percent S, the average sulfur content at this point is 0.0325 percent. 166 lbs of slag is considered an entirely adequate amount for desulfurization and operating experience might well indicate that good results can be obtained with a smaller slag volume.

In this operation it might not be necessary to reduce the oxygen activity to 0.5. It was assumed that the slag additions would immediately melt and be in equilibrium with the melt. If it takes several minutes for FeO to build up in the slag at oxygen activities higher than 0.5, than an oxygen activity of 0.85 during slag meltdown may be employed.

By assuming the calculated 166 lbs. of slag are needed for desulfurization, an additional 130 lbs. of CaO + SiO₂ are needed. Slag meltdown is accomplished by the superheat. Enough natural gas is blown to keep the tuyeres open and result in good bath-slag mixing.

During this slag meltdown, oxygen and natural gas are blown at ratios of 0.83 (melt oxygen activity = 0.5) and will release 22,400 Btu/lb atom-contained carbon in natural gas.
### Operation 6. Slag is Decanted

Depending upon the kinetic and enthalpy requirements of FeO reduction from the slag, it may be advantageous to decant the slag after the final superheat.

### Operation 7, 8 and 9. Superheat and Final Carbon Adjustment

After the slag has been decanted, the oxygen activity is increased to about 0.95 for efficient utilization of the natural gas during superheating to 3000°F. At this point, the bath is re-carburized to 0.01 to 0.03% C with natural gas.

The metal in the vessel, without about 0.03 percent carbon can be further increased in carbon content by continuous blowing with natural gas. However, above 0.04 percent carbon, solid carbon or graphite injection with a carrier gas is advantageous for re-carburization of the melt.

### Operations 10 and 11. Tap Leaving Heel of Molten Metal and Vessel Inspection

A summary of the cycle operation is shown below:

<table>
<thead>
<tr>
<th>Estimated Time to Accomplish Operation (Minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1040 lbs of scrap added to 1040 lbs. of</td>
</tr>
<tr>
<td>charge (might need one or two</td>
</tr>
<tr>
<td>more charges). Heel will contain 0.07 to</td>
</tr>
<tr>
<td>0.10% carbon</td>
</tr>
<tr>
<td>2. Meltdown of scrap and formation of</td>
</tr>
<tr>
<td>Slag No. 1 takes place. Variation in</td>
</tr>
<tr>
<td>melt-down time due to preheat</td>
</tr>
<tr>
<td>3. Initial superheat in preparation for</td>
</tr>
<tr>
<td>deoxidation</td>
</tr>
<tr>
<td>4. Partial deoxidation of melt by reducing</td>
</tr>
<tr>
<td>oxygen to N.G. ratio to about 0.5 Melt</td>
</tr>
<tr>
<td>oxygen activity reduced to 0.83. See Table 5.</td>
</tr>
<tr>
<td>FeO in slag is reduced from 151 lb/t on metal</td>
</tr>
<tr>
<td>to 24.8 lb/t of metal.</td>
</tr>
<tr>
<td>5. Addition of desulfurizing slag components.</td>
</tr>
<tr>
<td>CaO and SiO2 added. Oxygen activity in melt</td>
</tr>
<tr>
<td>decreased to 0.3. Oxygen to N.G. ratio is</td>
</tr>
<tr>
<td>0.83, 0.05% C in bath.</td>
</tr>
<tr>
<td>6. Slag is decanted</td>
</tr>
<tr>
<td>7. Final superheat to 3000°F (or any other</td>
</tr>
<tr>
<td>desired temperature). Oxygen activity is</td>
</tr>
<tr>
<td>increased to 0.95 during superheat</td>
</tr>
<tr>
<td>8. Initial re-carburization to 0.04% C with</td>
</tr>
<tr>
<td>natural gas</td>
</tr>
<tr>
<td>9. Final carbon adjustment by injection of N.G.</td>
</tr>
<tr>
<td>and carbon into the bath to bring the melt</td>
</tr>
<tr>
<td>carbon up to desired level (say 0.08%)</td>
</tr>
<tr>
<td>10. Tap leaving heel of molten metal. Cover</td>
</tr>
<tr>
<td>ladle with vermiculite. A small amount of</td>
</tr>
<tr>
<td>slag can then be used to form a ladle cover</td>
</tr>
<tr>
<td>11. Vessel inspection</td>
</tr>
<tr>
<td>Total cycle time</td>
</tr>
</tbody>
</table>

We claim:

1. A method for melting and refining solid ferrous scrap metal which comprises:
   a. providing a molten pool of ferrous scrap metal containing less than about 1 percent carbon by weight;
   b. introducing a charge of solid ferrous metal containing an average of less than about 1 percent carbon by weight into said molten pool;
   c. introducing into said molten pool at one point an amount of an oxidizing composition which contains from about 20 percent to 100 percent oxygen available for reaction;
   d. introducing into said molten pool at another point a fuel in such a ratio to the oxidant that an exothermic reaction occurs predominantly below the surface of the molten pool which is substantially neutral or only mildly reducing to iron oxide and which releases sufficient heat of reaction to melt the feed ferrous scrap metal;
   e. recarbonizing the molten ferrous metal with an amount of carbon which is sufficient to impart a carbon content to the melt to produce steel and f. withdrawing at least a portion of the molten steel.

2. The method of claim 1 wherein the charge contains sulfur and substantially all or a part of said sulfur is removed by adding slag forming substances to the molten ferrous metal of step (c) and simultaneously therewith, reducing the ratio of oxygen to fuel to a level whereby the reaction of oxygen and fuel will remain exothermic but the formation of iron oxide will be substantially avoided, maintaining the reduced oxygen activity throughout the entire period of slag formation and upon removal of the slag restoring the ratio of oxygen to fuel to the previous level.

3. The method of claim 1 wherein the molten pool of ferrous metal of step (a) is the heel of molten steel from the previous heat sufficient in volume to accomodate the feed ferrous metal.

4. The method of claim 1 wherein the ratio of oxidant to fuel is adjusted from the initial condition in which the reaction of oxidant and fuel yields neutral or only mildly reducing gases to a condition in which the reaction yields a sufficient quantity of reducing gas to reduce excess iron oxide to metallic iron.

5. The method of claim 1 wherein the combustible off-gases generated by the system comprising in major portion hydrogen and carbon monoxide are burned and the heat of combustion therefrom utilized for preheating one or more of the components introduced into the system.

6. The method of claim 5 wherein the feed ferrous metal is preheated and the burning of the off-gases is accomplished in a series of steps such that the temperature of the feed ferrous metal increased during heating, the scrap is exposed to combustion gases.

7. The method of claim 5 wherein the fuel is preheated.

8. The method of claim 5 wherein the oxidant is preheated.

9. The method of claim 1 wherein the feed source is part or all scrap steel containing about 0.1 percent carbon by weight.

10. The method of claim 1 wherein the oxidant is high purity oxygen.

11. The method of claim 10 wherein the oxidant is introduced into said molten pool at a pressure of from about 50 to about 150 p.s.i.a.

12. The method of claim 1 wherein the oxidant is oxygen-enriched air in which the concentrations of nitrogen does not adversely affect the resulting steel.

13. The method of claim 1 wherein the fuel is a hydrocarbon fuel.

14. The method of claim 13 wherein the fuel is natural gas or reformed natural gas.

15. The method of claim 1 wherein the oxidant is high purity oxygen and the fuel is natural gas.

16. The method of claim 15 wherein the high purity oxygen is lanced into the molten pool from above the surface thereof and the natural gas is introduced into the molten pool from the bottom thereof.
17. The method of claim 15 wherein both the high purity oxygen and the natural gas are lanced into the molten pool from above the surface thereof.

18. The method of claim 15 wherein both the high purity oxygen and the natural gas are introduced into the molten pool from the bottom thereof.

19. The method of claim 15 wherein a portion of high purity oxygen is mixed with the natural gas prior to the introduction thereof into the molten pool, the quantity of oxygen in the mixture being below that at which spontaneous combustion of the mixture under the prevailing conditions of the system can take place.

20. The method of claim 1 wherein recarbonization of the molten ferrous metal is accomplished by increasing the amount of fuel relative to the oxidant; blowing fine solid carbon or carbon-containing solid suspended in the fuel stream into the molten pool; utilizing a hydrocarbon fuel having a high carbon to hydrogen ratio or utilizing the carbon which is produced by the cracking of a hydrocarbon fuel.

21. The method of claim 1 wherein at least a portion of the off-gases generated by the system containing substantial quantities of hydrogen and carbon monoxide are recycled into the molten pool via the fuel stream.

22. The method of claim 1 wherein recarbonization of the molten ferrous metal is accomplished by increasing the amount of fuel relative to the oxidant; blowing fine solid carbon or carbon-containing solid suspended in the fuel stream into the molten pool; utilizing a hydrocarbon fuel having a high carbon to hydrogen ratio or utilizing the carbon which is produced by the cracking of a hydrocarbon fuel.

23. The method of claim 22 wherein recarbonization is accomplished by utilizing the carbon produced from the cracking of a hydrocarbon fuel and at the same time recarbonization is in progress, blowing the oxidant across the surface of the melt to cause combustion of off-gas which imparts heat to the bath thus minimizing the chilling effect of the endothermic hydrocarbon fuel cracking reaction.

24. The method of claim 23 wherein the hydrogen gas which is produced from the cracking of the hydrocarbon fuel is removed from the molten steel by injecting a sufficient quantity of carbon dioxide into the steel just prior to the withdrawal of the steel.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,772,000 Dated November 13, 1973

Inventor(s) Richard W. Hyde; Herman P. Meissner; Charles L. Kusik

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

Column 6, Line 25, "exchanger 7" should read --exchanger 77--
Column 8, Line 36, "overall" should read ---overall--
Column 15, Line 2, "and no prevent" should read --and to prevent--
Column 16, Line 56, "activity of 0.85" should read -- activity of 0.83--
Column 17, Line 14, "without about 0.03 percent" should read -- with about 0.03 percent--

Signed and sealed this 16th day of April 1974.

(SEAL)
Attest:

EDWARD H. FLETCHER, JR.
Attesting Officer

G. MARSHALL DANN
Commissioner of Patents