Dec. 8, 1965

[45] May 16, 1971

[54]	PROCESS FOR MANUFACTURE OF PIGIRON OR STEEL		
[72]	Inventors:	Hermann Rüter, deceased, late of Ludwigshafen, Rhine, Germany by Elisabeth Rüter and Edla Rüter, heirs; Egon Cherdron, Limburgerhof Palatenate; Manfred Haerter, Ludwigshafen Rhine; Gerhard Bayer, Ludwigshafen-Rheingonheim, all of Germany	
[73]	Assignee:	Gebr, Giulini G.m.b.H., Ludwigshafen/Rhine, Germany	
[22]	Filed:	Nov. 25, 1969	
[21]	Appl. No.:	879,830	
	R	elated U.S. Application Data	
[63]	Continuation-in-part of Ser. No. 599,409, Dec. 1966, abandoned.		
[30]	Fore	gign Application Priority Data	

[58] Field of Search......75/38

Germany......G 45389

[56]	References	Cited	

1,871,848	8/1932	Gustafsson	75/38 X
2,526,658	10/1950	Harman et al	
2,526,659	10/1950	Harman	
3,205,065	9/1965	Mayer et al	
3,295,958	1/1967	Rüter et al	75/38
2,806,779	9/1957	Case	
3,153,588	10/1964	Madaras	

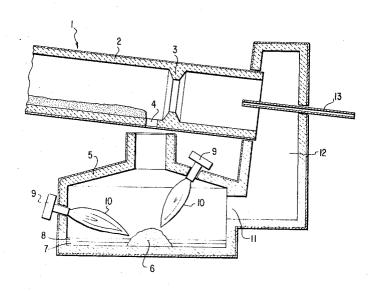
UNITED STATES PATENTS

Primary Examiner—Henry W. Tarring, II Attorney—Spencer & Kaye

## [57] ABSTRACT

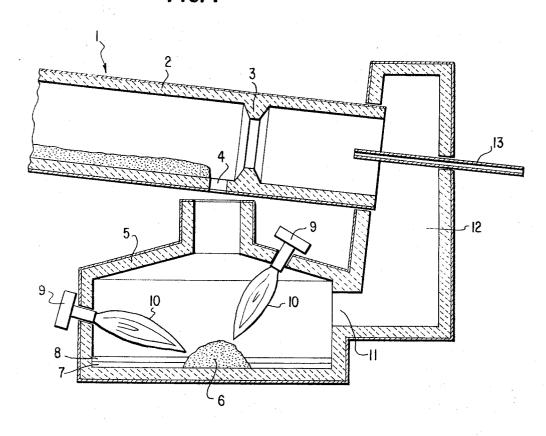
A two-stage method for the reduction of iron-oxide-containing raw materials wherein the iron oxide is reduced by means of solid carbonaceous material in a first stage carried out in a rotary kiln. The raw materials issue from the kiln in the form of a partially reduced sinter containing at least 5 percent free carbon. Reduction is completed in a second state carried out in a direct-fired smelting furnace, where a part of the free carbon in the sinter is burned by hot, oxygen-containing exhaust gases of the direct-fired smelting furnace to effect a temperature rise to smelt the sinter from the first stage.

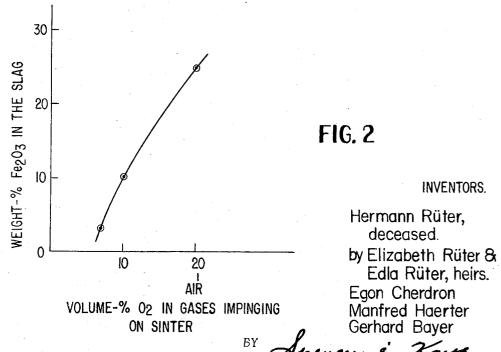
10 Claims, 2 Drawing Figures



ATTORNEYS.

FIG. I





# PROCESS FOR MANUFACTURE OF PIG IRON OR STEEL

# CROSS-REFERENCES TO RELATES APPLICATIONS

This is a continuation-in-part to our copending application U.S. Ser. No. 599,409, filed Dec. 6, 1966, for a "Process for Manufacture of Pig Iron or Steel", now abandoned.

# BACKGROUND OF THE INVENTION

The present invention relates to a novel process for the 10 manufacture of pig iron or steel from ores or waste materials containing iron oxides.

In producing metallic, zero-valent iron from iron oxide, all of the so-called shaft furnaces require lumps of coke. These lumps serve as the heating fuel. They also have the second 15 function of helping to form a stable, gas-permeable stock. When hot air (perhaps enriched with oxygen) is blown into the stock at the lower end of the shaft, the coke at such location is burned. There is a sharp increase in temperature and the O<sub>2</sub> reacts quantitatively to form CO<sub>2</sub>. This CO<sub>2</sub>, along with 20 other gaseous components such as nitrogen, proceeds to move upwards through the stock. Within a short distance, by contact with glowing coke, the CO2 has reacted quantitatively to form CO according to the formula

$$CO_2 + C = 2CO. (1)$$

In the classical blast furnace process, the CO thus formed has a very important task, namely to reduce the iron ore according to the formula

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

As is evident from formula (2), CO<sub>2</sub> is again formed. This CO<sub>2</sub> 30 tends to react with coke higher in the stock to form more CO according to equation (1). Thus, the gases leaving shaft furnaces are very high in CO. If the iron oxide charge to these shaft furnaces is intimately mixed with fine carbon particles, such as is taught in U.S. Pat. No. 2,988,442 issued to G. 35 Tanner on June 13, 1961, for "Reduction of Iron Ore by Hydrocarbons," the present inventors have determined that the CO in the gases leaving a shaft furnace is even higher than is the case where only lump coke is present. The same is true if the shaft furnace charge is the char-bonded pellets taught by S.L. Case in U.S. Pat. No. 2,806,779, issued Sept. 17, 1957, for a "Method of Producing Iron."

As is evident from the above-related features of shaft-furnace operation, the energy for heating the charge to shaft furnaces and for reducing such is supplied by heat transfer from 45 hot gases originating in the stock at the tuyeres and flowing upwards over the individual pieces of the stock. This mode of operation necessarily leads at the level of the tuyeres to an overheating of slag and iron droplets and to a carburizing of the iron.

#### SUMMARY OF THE INVENTION

The present inventors considering the high CO content of the stack gases of shaft furnaces, especially the high CO resulting when charging with the products of the Tanner and Case patents, to represent a waste of heat which would be available by complete oxidation of carbon and to represent a potential health hazard, one object of the present invention is to provide a process for producing zero-valent iron wherein partially 60 reduced, carbon-containing, iron oxide material resembling the shaft-furnace charges of the above-mentioned Tanner and Case patents can be terminally reduced with relatively little CO in the off-gas.

method for reducing charges resembling those of the Tanner and Case patents without requiring the use of the expensive lump coke required for shaft furnace operation.

Another object of the present invention is to provide a method for finally reducing charges resembling those of the 70 Tanner and Case patents without of necessity producing an overheating of slag and molten iron and an increased carburizing of the iron.

Another object of the present invention is to provide a

the Tanner and Case patents characterized by a high-speed smelting of the partially reduced charge, whereby smelting furnace size can be minimized for a given production rate.

Another object of the present invention is to provide a process for producing a partially reduced, carbon-containing charge resembling those of the Tanner and Case patents but differing from them in essential aspects, whereby shaft-furnace final reductions may be avoided and the above objects

These as well as other objects which will become apparent in the discussion that follows are achieved, according to the present invention, by a two-stage process which is summarized in the following two paragraphs.

In accordance with the present invention, there is provided a novel process for the manufacture of molten pig iron or steel from iron-oxide-containing by-products or iron ores. In the first stage, the iron-oxide-containing starting material is reduced in conventional manner with an excess of a solid carbonaceous reducing agent, such as, for example, coal, coke, coke breeze, or other solid carbonaceous materials or wastes, in a rotary kiln, to produce a sinter containing at least about 5 percent, and preferably from about 8 to 12 percent, of free carbon. The reaction takes place in accordance with the equa-

$$Fe_2O_3 + 3C = 2Fe + 3CO.$$
 (3)

The temperature of the reaction is maintained below that of the melting point of the reduced or partly reduced mass, advantageously at about 900° to 1,100° C., so that the degree of reduction of the Fe<sub>2</sub>O<sub>3</sub> to Fe amounts to 70 to 95 percent, and preferably about 80 to 92 percent, with the reduced sinter still containing free carbon in finely divided form to the extent of at least 5 percent, preferably about 8 to 12 percent.

The second stage of the method of the invention comprises bringing the sinter obtained in the first stage into contact with an oxygen-containing gas, the sinter being advantageously at a temperature of at least about 800° C., and preferably about 900° to 1,100° C., so that a selective combustion of a part of the excess carbon takes place, with the objective of producing a strongly spontaneous local rise in temperature and thereby an instantaneous smelting of the iron. The oxygen-containing gas is brought so intimately into contact with the sinter, the gas being itself at a temperature above about 1,200° C., and preferably above 1,400° C., that a selective combustion of a portion of the excess carbon occurs, thereby achieving a sudden strong rise in temperature accompanied by a melting and a reduction of the unreduced iron oxide within a period of a few seconds.

# BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevational cross section through part of an apparatus preferred for performing the method of the invention. FIG. 2 is a graphical representation of the relationship between two parameters of the present process. See Examples

3 to 5.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The apparatus preferred for carrying out the method of the present invention is of the type shown in U.S. Pat. No. 2,526,658 issued to E.S. Harman et al. on Oct. 24, 1950, for a "Process for Smelting Iron Ore" and this patent is therefore Another object of the present invention is to provide a 65 incorporated into the present disclosure by reference for the purpose of relating the presently disclosed method in relationship to apparatus for carrying it out.

The first-stage reduction of the iron-oxide-containing starting material with solid carbonaceous agents is carried out in a continuously operating rotary kiln, such as kiln 10 of the Harman patent.

The choice of the proportion of iron-oxide-containing material to solid carbonaceous reduction agent may vary widely, depending upon the nature of the material being process for the final reducing of charges resembling those of 75 reduced and the residence time in the reduction furnace.

As is well known, in the reduction of iron ores in rotary kilns a certain proportion of the carbon reducing agent is lost through contact with the oven atmosphere. This loss of carbon depends upon a number of factors, such as the speed of rotation of the kiln, the length of the kiln, the depth of the bed of iron oxide material and its physical condition, and the like. Accordingly, the amount of carbon required must be carefully adjusted, and precautions taken that after the reduction there still remains in the sinter at least 5 percent, and preferably about 8 to 12 percent, of free carbon, calculated upon the weight of the sinter, since this carbon serves as the fuel for the smelting of the sinter. It is important that the solid carbonaceous reducing agent used in the present invention be low in volatiles, so that larger particles thereof can pass through the first-stage rotary kiln treatment without becoming crumbly and disintegrating into smaller particles.

Complete reduction in the rotary kiln is not required, and in practice this is difficult to attain in any case. Especially is this difficult when the raw material has a low iron content, e.g. 35% Fe. Nevertheless, 70 to 95 percent, and preferably 80 to 92 percent, of the iron oxide should be reduced to metallic iron in the rotary kiln.

The starting material in the form of a mixture of iron oxide, slag forming constituents such as limestone, and solid carbonaceous material is advantageously prepared for charging to the kiln by fine grinding and intimate mixing of its components to obtain a homogeneous mass and then forming therefrom particles having a size of about 3 to 30 mm, which This can be accomplished through graining or briquetting of the finely ground starting material. By "fine grinding" meant size reduction such that more than 50 percent of the material has particle sizes below 0.1 millimeters, while particles of size greater than 0.1 mm remain and there are no parti- 35 cles of size greater than 2 mm. In case the iron-oxide-containing material is available in very moist form, or even as a mud, wet grinding can also be used, and the mud can be dried in conventional manner so that dry solid granules are produced. For example, the drying can be performed in the rotary kiln 40 used for the reduction by equipping the kiln with suitable fittings for mud drying.

Nevertheless, the preparation of a mixture by fine grinding and forming is not absolutely necessary for the present invention. In the case of readily reducible iron ores, the objects of 45 the invention can be achieved by employing only coarsely ground, nonformed starting materials.

It will be apparent that the rotary kiln can also be operated where only a portion of the required carbonaceous reducing agent has been mixed with the charge, and that a reducing gas can be employed to replace the missing portion of the carbonaceous agent.

During the reduction in the rotary kiln, the smallest carbonaceous particles, because of their lower effective heat 55 capacity, undergo temperature rises more easily and react first with the iron oxide while coarser carbonaceous particles because of their larger effective heat capacity, only suffer some slight attack on their surfaces. Consequently, the carbonaceous particles in the sinter product issuing from the rotary kiln lie essentially in the visible size range of about 0.1 to 2 mm, the minus 0.1 mm particles having been consumed. It is important that the operation of the first stage in the rotary kiln be such that these solid carbonaceous particles in the visible size range end up present in the sinter issuing from the kiln. It 65 has been found that, otherwise, the instantaneous smelting characterizing the second stage treatment in the stationary smelting furnace is not achieved.

As in the case of the Harman patent, kiln temperatures and holding times are regulated so that the kiln charge leaves the 70 kiln in the form of a sinter. This sinter falls as shown in FIG. III of the Harman patent onto the hearth of a stationary smelting furnace such as furnace 11 of Harman.

The sinter, as it leaves the kiln, has a temperature of about

percent, preferably 8 to 12 percent, free carbon. The free carbon is in the above-mentioned visible size range.

A unique feature of the method of the present invention lies in impinging the sinter on the hearth of the stationary smelting furnace with hot, oxygen-containing gases, whereby the free carbon instantly reacts with the oxygen and produces smelting in a matter of moments.

The hot, oxygen-containing gases required for the process can be produced by the combustion of liquid or gaseous fuels with excess air such that, when combustion ceases, the exhaust gas contains by volume at least 3 percent, preferably at least 5 percent, at most 12 percent, preferably at most 10 percent oxygen at a temperature of at least 1,400° C. In practice, the impinging is achieved by directing the flames of burners placed at the position of burners B in the Harman patent toward the sinter on the hearth and regulating the reach of the flames such that burning ceases just as the hot gases reach the sinter.

Care must be taken that the exhaust gas makes good contact with the sinter, in order to avoid loss of the furnished oxygen to the off-gases, before it has had a chance to react with the carbon. The practice of directing the flames of the burners directly at the sinter helps to achieve this good contact.

With the impingement of the oxygen-containing exhaust gas onto the sinter, a portion of the residual carbon burns. The heat developed by this burning melts the sinter and, at the same time, a final reduction of iron oxide occurs. The burning is predominently to CO2, rather than CO. CO produced by the form it will retain, for the most part, following the reduction. 30 reduction burns to CO2. This leads to a heat evolution more than three times higher than that which would be obtained for CO, as is evidenced by the following:

$$C + O_2 = CO_2 (\Delta H_{298} = 7944 \text{ kcal/kg}),$$
 (4)  
 $C + 1/2O_2 = CO (\Delta H_{298} = 2302 \text{ kcal/kg}).$  (5)

It has been found, in accordance with the present invention, that for the second stage of the process, a stationary directfired smelting furnace such as furnace 11 of the Harman patent, is most suitable. In a furnace of this type, the conditions required for the smelting of the reduced sinter can be maintained most precisely. Owing to the fact that in a stationary, direct-fired smelting furnace the reduced sinter introduced rests on the furnace floor or on the slag-iron-bath, until it is smelted, granules and larger pieces can be handled, just as advantageously as in the preceding rotary kiln. Such larger pieces can be smelted with certainty. Such is practically impossible in a cyclone or vortex furnace.

A further advantage of the stationary smelting furnace lies in that, in order to protect the furnace wall against attack by slag, only a very small portion of the furnace wall, namely that portion which is in contact with the liquid slag, needs to be cooled, so that this limited zone can safely be protected with a layer of solidified slag. The limited size of this cooled portion means that very little heat is lost through cooling.

A further advantage of the stationary direct-fired smelting furnace lies in that its operation is extremely simple. In a rotary kiln the tapping of the slag and the iron is much more difficult to perform than in a stationary furnace. In the case of vortex and cyclone furnaces, the openings through which the burners extend into the interior can become crusted with slag. This is impossible in a stationary direct-fired smelting furnace, since, in contrast to other types of furnaces, the molten slag and the molten iron rest on the hearth. This permits the complete separation of the iron and the slag, whereas with the other types of furnaces, an additional, generally heated, forehearth is necessary for complete separation of iron and

A great advantage of the stationary direct-fired smelting furnace is that slag, in molten form and cleanly separated from the iron, can be tapped in such manner that it can be further processed as desired. For example, by blowing with steam or air or by spinning, slag fibers or slag wool can be prepared, both of which are valuable by-products.

The term "direct-fired smelting furnace," as employed 900° to 1,100° C. It contains finely divided iron and at least 5 75 herein, designates a hearth furnace in which the sinter introduced is heated and melted by the action of flames which extend toward the material. Thereby heat transfer takes place through conduction, convection and radiation from the gas flames and hot exhaust gases to the sinter. Ordinarily such operation would require very long smelting times, which in turn would mean relatively large furnace capacities. However, in accordance with the present invention, the heating of the sinter charged from the kiln is furthered to a considerable extent by combustion of excess carbon in the sinter, whereby owing to the direct contact of the burning carbon with the reduced ore, a considerably more rapid heat transfer takes place than would result from heat coming from flames and gases alone. Consequently, the size of the furnace is only a fraction of the size of a conventional direct-fired furnace having an equal production rate.

The flames of the burners of the direct-fired smelting furnace are only indirectly concerned with the smelting of the sinter. The flames, in general, serve on the one hand to convert the fuel-air mixture into hot oxygen-containing exhaust 20 gas to produce rapid combustion of the excess carbon in the sinter. The fuels for the combustion mixture may be gaseous or liquid. On the other hand, the flames maintain the walls of the furnace at the desired temperature, i.e., they compensate for radiation to the exterior, so that the heat of combustion of 25 the carbon in the sinter is practically all available for the melting of the iron and slag and for carrying out the reduction of the remaining iron oxide.

As will be apparent from the foregoing description, it is possible, in accordance with the present invention, to operate the burners of the smelting furnace with air at ambient temperature, e.g. 20° C, but nevertheless to smelt the sintered charge within a short time. This fact is extraordinarily surprising when one takes into account that, for example, in the smelting of high analysis ores in a blast furnace, the air must be heated to at least 800° C. to produce the necessary iron temperature. The use of air at ambient temperature is an advantage of the present invention which should not be underestimated.

The liquid slag and iron in the smelting furnace can be withdrawn separately. Suitable apparatus for collecting and separating iron and slag is disclosed in the Harman patent. The exhaust gases of the smelting furnace have a temperature of about 1,500° C as they leave the furnace and are introduced 45 into the rotary kiln to heat the latter. The Harman patent shows a suitable connection of kiln 10 and furnace 11 to accomplish this utilization of the smelting furnace exhaust gases.

The extraordinary economic and industrial advantages of the invention may be summarized as follows:

- 1. The process can utilize all sorts of iron ores, including not only high analysis ores, but also medium range ores which hitherto could not be processed economically in conventional iron recovery processes because of their high slag output. Moreover, with the method of the present invention, the difficulty workable fine ores can be successfully treated, including the so-called red mud, which is the residue resulting from the preparation of alumina by the Bayer process. The processing of red mud economically to recover useful pig iron therefrom was not possible prior to the present invention. The process of the invention is industrially and economically practicable, and it is surprisingly found that the pig iron obtained is completely free from contaminating elements, particularly titanium, vanadium, chromium, and especially manganese and 65 silicon, so that it is suitable for special purposes.
- 2. Cheap waste coals, coal fines, coke fines, and the like may be employed for reduction. Since the excess of reducing carbon required for the reduction is burned in the smelting furnace, a large part of the additional heat energy needed for 70 smelting is saved.
- 3. As supplemental fuels for maintaining the smelting furnace temperature there can be utilized cheap liquid or gaseous fuels, in contrast to the expensive coke pieces required for other iron recovery processes.

- 4. Smelting in the above-described direct-fired smelting furnace has the additional advantage that the slag can be directly spun or blown from the furnace, enabling the production of valuable by-products.
- 5. The air required for smelting usually does not need to be preheated; it suffices to mix ambient-temperature air with fuel in such ratio that, when burning ceases, the exhaust gas has a temperature of at least 1,200° C, preferably at least 1,400° C, and an oxygen content of at least 3 percent, preferably at least 10 5 percent, at most 12 percent, preferably at most 10 percent.

The following examples illustrate the practice of the invention, but are not to be regarded as limiting:

#### EXAMPLE 1

#### Treatment of Iron Ore

A mixture was prepared, consisting of 100 parts by weight of an iron-oxide-containing wet concentrate with:

52.3 %	Fe <sub>2</sub> O <sub>3</sub>
15.1 %	SiO <sub>2</sub>
6.5 %	Al <sub>2</sub> O <sub>3</sub>
3.8 %	CaO
1.5 %	MgO
20.0 %	H <sub>2</sub> O

20 parts by weight of calcium carbonate, 30 parts by weight of mud coal with:

69.0 % 18.5 % 4.0 % 6.2 %	carbon water volatile constituents ashes
0.2 //	asiles
	18.5 % 4.0 %

The mixture was ground in a tube mill to minus 2 millimeter particle size and then charged at a rate of 12 tons per hour into a rotary kiln of 100 m length and 1.8 m diameter. Inside the rotary kiln the charge was dried, and 82.5 percent of the ironoxide was reduced to metallic iron at a maximum temperature of 1,050° C; no melting of the mixture occurred.

The sintered reduced product, containing 8.2 percent carbon, was continuously charged into an oil-fired, round smelting furnace of 20 square meters internal hearth surface immediately after leaving the rotary kiln with a temperature of 1,000° C. Eight burners were mounted on the cylindrical side wall of the furnace and so directed, that the exhaust gases of their flames impinged directly on the sinter charged in the middle of the hearth surface. The flames were adjusted so that their tips were on a time average about 2.5 centimeters from the sinter. The oil and air mixture of the burner was so adjusted, that the exhaust gases at the tips of the flames contained 8 percent by volume O2. Because of the immediate reaction of this hot oxygen with the hot carbon of the sinter, a spontaneous melt down of the rotary kiln-discharge occurred, whereby a temperature of 1,580° C built up in the liquids inside the smelting furnace, thus causing the separation of iron and slag into two distinct liquid phases, the slag flowing continuously out of an opening on the side of the smelting furnace. The liquid iron was cut off periodically. By determining the iron-content of the slag, it was found that 96.2 percent of the iron was recovered in the zero-valent state. This iron contained 2.5 percent carbon and 0.2 percent sulphur, while other elements only existed in traces under 0.01 percent. The flue gas of the smelting furnace blown into the reduction furnace contained, by volume, 17.5% CO<sub>2</sub> and 0.5% CO.

## EXAMPLE 2

## Treatment of Red Mud

An iron-oxide-containing red mud, i.e. the residue resulting from the preparation of alumina by the Bayer process, had the following analysis:

26.1 %	Fe <sub>2</sub> O <sub>3</sub>
9.1 %	Al <sub>2</sub> O <sub>3</sub>
4.5 %	SiO <sub>2</sub>

2.6 %	* *	TiO.
3.2 %		Na₀Ô
4.0 %		loss at red heat
50.0 %		H <sub>2</sub> O

The wet mud was mixed in a proportion of:

100 parts	red mud
10 parts	ground limestone
15 parts	mud coal

-said mud coal having the analysis described in Example 1and in a quantity of 16.5 tons per hour apportioned to a rotary kiln (length 100 m, diameter 1.8 m). Inside the rotary kiln the muddy mixture was dried and 84 percent of the iron-oxide was reduced to metallic iron at a maximum kiln temperature of 15 1,070° C. The reduced sinter, comprising remainder 7.8 percent carbon, fell into the oil-fired smelting furnace of Example 1 at a temperature of 1,040° C. The oil and air mixture was so proportioned that the gases at the tips of the flames still contained 9 percent by volume O<sub>2</sub>. The melt down took place in <sup>20</sup> the same way as described in Example 1. By determining the iron-oxide content of the slag, it was found that 97.2 percent of the iron was recovered in the zero-valent state. The iron produced this way contained 2.2% carbon and 0.25 percent 25 sulfur. Other elements could only be found in quantities under 0.02 percent. The flue gas of the smelting furnace blown into the reduction furnace contained, by volume, 17.0% CO<sub>2</sub> and 0.7% CO.

#### **EXAMPLES 3 TO 5**

In order to show the importance of the oxygen content in the gases impinging on the sinter on the smelting furnace hearth, three tests were made using essentially the process was varied. Air was used for the highest-oxygen test. The results are shown in FIG. 2 of the drawings. It will be noted that a reoxidation occurs for 20 percent oxygen, the iron oxide increasing from 20 percent in the sinter to 25 percent in the slag, these percentages of iron oxide being based on the weight of the slag as 100 percent. At 10 percent oxygen in the impinging gases, the iron oxide content in the slag decreased to 10 percent, while for impinging gas containing 7 percent oxygen, a slag with an iron oxide content of 3 percent was achieved. Of course, the oxygen should not be reduced below 3 percent, since then the instantaneous smelting characteristic of the present invention is not achieved.

#### **EXAMPLE 6**

The conditions were same as in Example 2, however, with the following differences:

Instead of 15 parts mud coal only 12 parts were added. In addition 250 kgs per hour oil were sprayed into the kiln from its end opening. Kiln-temperature: 960° C maximum. Temperature of sinter when falling into the smelting furnace: 950° C. Carbon-content in sinter: 8.3 percent. Degree of reduction: 90.5 percent. The yield of metallic iron in the smelting furnace amounted to 95.5 percent. The iron produced this way contained 2.3 percent carbon and 0.7 percent sulphur.

While a stationary smelting furnace such as furnace 11 of the Harman patent has been used successfully for the process of the present invention, it is also possible to apply a rotary smelting furnace such as that described, for instance, in "The Mining Magazine," September 1951, pages 144-146.

As mentioned above, the preferred apparatus for performing the method of the present invention resembles the apparatus described in U.S. Pat. No. 2,526,658, FIG. 3. However, in contrast to the apparatus and the mode of operation described therein there are the following differences inherent 70 in the present invention.

According to U.S. Pat. No. 2,526,658 the reduced iron ore

is overheated to an extent, that it turns pasty. Thereby the reduced iron becomes nodulized. Furthermore deposits build up in the rotary kiln, which have to be removed by boring bars. In conformity with the present process the reduced sinter 5 still containing 8-12 percent carbon is not heated until it starts smelting, therefore, no deposits build up on the kiln walls.

According to U.S. Pat. No. 2,526,658 the burners A are arranged to produce an exhaust gas in which the relation of CO2: CO approximates 8:1. In conformity with the present inven-10 tion the burners are arranged strongly oxidizing, so that the exhaust gas contains no CO at all but at least 3% O2.

The reducing burners B are not necessary.

It is not necessary to blow in carbon at C and D.

FIG. 1 illustrates preferred apparatus for performing the method of the invention. 1 is the lower end of a rotary kiln in which Fe<sub>2</sub>O<sub>3</sub> is reduced as known. 2 = masonry lining. 3 = baffle ring. 4 = opening for removing the reduced material. 5 is the masonry lined smelting furnace to the bottom of which the reduced sinter is brought through 4 to form pile 6. 7 = molteniron. 8 = molten slag. 9 = burners the flames 10 of which end shortly in front of 6. The exhaust gas from the flames impinges onto the outside of pile 6. 11 = opening for withdrawal of exhaust gas. The exhaust gas is led through a channel 12 to the rotary kiln. Alternatively oil may be sprayed into the rotary kiln through a pipe 13.

Unless indicated otherwise, all percentages given above are based on weight.

It will be understood that the above description of the present invention is susceptible to various modifications, 30 changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

We claim:

1. A method for reducing iron-oxide-containing material to conditions of Example 1, except that the amount of oxygen 35 a zero-valent iron product, comprising the steps of producing a sinter of said material and at least 5 percent solid carbonaceous material in the particle size range of 0.1 to 2 millimeters, 70 to 95 percent of the total iron in the sinter being in the zero-valent state, the sinter having a temperature of at 40 least 800° C, forming said sinter into a pile in a stationary direct fired smelting furnace, impinging the outside of said pile of sinter with only exhaust gas from the combustion of a fuel with oxygen-containing gas, said exhaust gas having an oxygen content of 3 to 12 percent by volume and a temperature of at 45 least 1,200° C, for effecting a final reduction and a melting of said sinter, and collecting the molten product of the step of impinging in a zero-valent iron phase and a slag phase.

2. The method as claimed in claim 1, the step of producing including the passing of a mixture of said material with solid 50 carbonaceous material through a rotary kiln operated at 900° to 1,100°C.

3. The method as claimed in claim 1, the zero-valent iron in the sinter amounting to 80-92 percent of the total iron.

4. The method as claimed in claim 1, the solid carbonaceous 55 material in the sinter amounting to 8 to 12 percent.

5. The method as claimed in claim 1, said exhaust gas having an oxygen content of 5 to 10 percent by volume.

6. The method as claimed in claim 1, said exhaust gas having a temperature of at least 1,400° C.

7. The method as claimed in claim 2, the step of impinging including the steps of allowing said sinter issuing from said kiln to fall onto the hearth of a stationary smelting furnace and directing flames producing said exhaust gas at the sinter on the hearth.

8. The method as claimed in claim 2, the step of producing further including a contacting of said mixture while in the kiln with a reducing gas.

9. The method as claimed in claim 1, wherein said material in the sinter is in the particle size range of 0 to 2 millimeters.

10. The method as claimed in claim 1, wherein said ironoxide-containing material is red mud.

# UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3	,663,202	Dated May 16th, 1972	
		Duter deceased From Chardren	
		Rüter, deceased, Egon Cherdron,	
Inventor(s)_	Manfred	Haerter and Gerhard Bayer	

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

Change the issue date of the patent on the title page, line 2, from "May 16, 1971" to --May 16, 1972--. In the ABSTRACT, line 6, change "state" to --stage--.

Signed and sealed this 24th day of October 1972.

(SEAL) Attest:

EDWARD M.FLETCHER, JR. Attesting Officer

ROBERT GOTTSCHALK Commissioner of Patents