

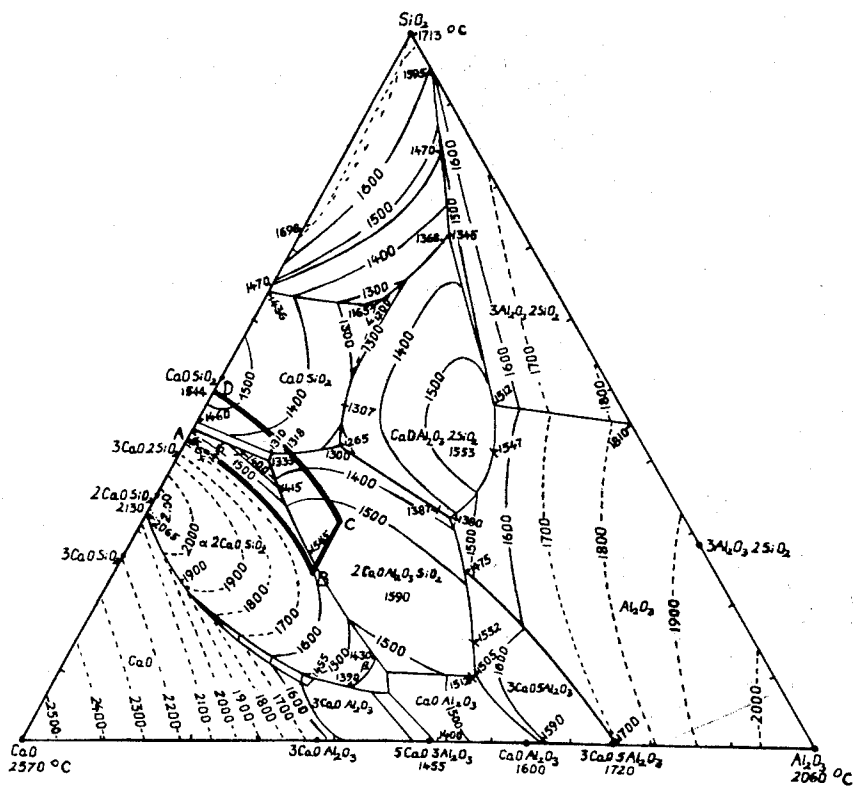
Sept. 22, 1964

S. MENNENÖH

3,149,962

METHOD OF PRODUCING FERROMANGANESE

Filed Jan. 4, 1962



System $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$

Inventor
Siegfried Mennenöh
by Michael S. Striker
Attorney

1

3,149,962

METHOD OF PRODUCING FERROMANGANESE
Siegfried Mennenöh, Hohenlimburg, Germany, assignor
to Hoesch A.G., Dortmund, Germany
Filed Jan. 4, 1962, Ser. No. 164,425
Claims priority, application Germany, Jan. 7, 1961,
H 41,405; Dec. 6, 1961, H 44,329
3 Claims. (Cl. 75-80)

The present invention relates to a method of producing ferromanganese, and more particularly, the present invention is concerned with a method of producing ferromanganese of relatively low carbon content.

It is possible without difficulties to produce ferromanganese of relatively high carbon content, for instance in a blast furnace or low shaft furnace, or also an electrically heated furnace. However, great difficulties are experienced when it is desired to produce ferromanganese of low carbon content, particularly of a carbon content below 1%. Such low carbon content ferromanganese is produced in electric arc furnaces which are charged with a mixture of manganese ore and ferrosilicon or silicon-manganese, or silicon-aluminum alloys, whereby a quantity of burnt lime is added which will suffice to give a basic compound with the silicon dioxide formed during the reaction. However, by proceeding in this manner one is faced with the additional difficulty that the slag will contain an extraordinarily large proportion of manganese. In order to remove this manganese from the slag or to reduce the manganese of the slag to a tolerable proportion, it is then required to extend the reaction time for greatly prolonged periods of time so that the silicon contained in the molten metal will reduce as much of the manganese of the slag as possible.

It is therefore an object of the present invention to overcome the above discussed difficulties.

It is another object of the present invention to provide a method of producing ferromanganese with relatively low carbon content which method can be carried out in a simple and economical manner.

It is a further object of the present invention to provide a method for producing ferromanganese having a carbon content of less than 1% which method can be easily and accurately controlled so as to give ferromanganese of the desired composition.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention contemplates in a method of producing ferromanganese, the step of reacting in a converter a mixture comprising the following components: (a) manganese ore having a MnO_2/MnO ratio greater than 1.1, (b) a reducing alloy consisting essentially of silicon and aluminum and having a Si/Al ratio of between 1 and 4, components (a) and (b) being present in such proportions that the oxygen content of the ore will be equal to between 90% and 110% of the amount of oxygen required for oxidation of said reducing alloy, and (c) burnt lime in an amount equal to between 40 and 60% of the combined weight of components (a) and (b).

According to a preferred embodiment of the present invention, the same comprises in a method of producing ferromanganese containing more than 70% manganese, between 0.06 and 1.0% carbon and between 1.5 and 10% silicon, the steps of forming a mixture of: (a) manganese ore having a MnO_2/MnO ratio greater than 1.1 and (b) a reducing alloy comprising silicon and aluminum in a combined amount of between 65 and 90% of which between one-half and one-fifth is aluminum, the balance comprising at least one of the elements iron, man-

2

ganese, titanium, calcium, carbon and impurities, components (a) and (b) being present in such proportions that the oxygen content of the ore will be equal to between 95% and 105% of the amount of oxygen required for oxidation of the reducing alloy, (c) and an amount of sulfur equal to between 0.8 and 4% of the weight of the manganese ore, introducing the thus-formed mixture and an amount of burnt lime equal to between 40 and 60% of the weight of the mixture into a dolomite-lined converter, igniting the mixture so as to cause reaction of the same forming a liquid bath and slag, and blowing gas through the liquid bath and the slag so as to intimately mix the same.

Thus, according to the present invention, ferromanganese of low carbon content may be produced in a converter in the following manner:

(1) Natural or partially roasted manganese ore, or a mixture of natural and partially roasted manganese ore, containing at least 1.1 parts of MnO_2 for each part of MnO , are mixed with a reducing alloy comprising silicon and aluminum in a combined amount of between 65 and 90% of such alloy, while the residue may consist of iron, manganese, titanium, calcium, carbon and conventional impurities. The amount of silicon in the reducing alloy is to be at least equal to, or up to four times as great as, the amount of aluminum thereof, and the ore and the reducing alloy are mixed in such proportions that the oxygen content of the ore will be equal to between 90% and 110% of the amount of oxygen required for oxidation of the reducing alloy.

Preferably, the MnO_2 content of the ore will be equal to between 1.25 and 2.5 times the amount of MnO therein, and the reducing alloy will contain between 45 and 55% silicon, between 20 and 30% aluminum and less than 0.8% carbon. Within these preferred proportions, the formation of ferromanganese will take place under optimum conditions due to adjustment of the thermodynamic processes involved and the slag composition relative to each other.

(2) The thus-formed mixture is charged into a bottom blown dolomite-lined converter with an addition of burnt lime equal to between 40 and 60% of the weight of the ore-alloy mixture.

(3) The mixture is ignited by priming and will react under formation of an intermediate metal bath consisting of manganese, silicon and iron, and of a slag rich in manganese.

(4) Thereafter, metal bath and slag are intimately mixed by blowing into the converter through the bottom thereof a preferably inert gas such as hydrogen or nitrogen. If the converter is sufficiently large, it is also possible to blow with oxygen-containing gases such as compressed air or water vapor-oxygen mixtures, due to the fact that in view of the relatively small amount of gas required for achieving intimate mixing of metal bath and slag, the oxidizing effect of the oxygen fraction of such gas is of minor importance. A metal bath is thus formed which will contain between 1.5 and 10% silicon, less than 1.0% carbon (generally less than 0.5% carbon), the carbon content of the metal bath depending to a considerable extent on the carbon content of the reducing alloy, and containing less than 0.01% sulfur. The iron content of the bath depends on the iron content of the charge and will be between 5 and 25%, the balance being manganese. The slag contains between 5 and 17% MnO , less than 22% Al_2O_3 and the lime content of the slag will be in the vicinity of the saturation point for dicalcium silicate. The temperature at the completion of the process will be between about 1,400 and 1,600° C.

When it is desired to produce ferromanganese containing less than 1.5% silicon, then, according to the

3

present invention, the slag is withdrawn and thereafter manganese ore and burnt lime are additionally introduced into the converter so that the excess of oxygen over the amount required for oxidation of the silicon will equal between 30 and 70%, and the contents of the converter are again intimately mixed preferably by an inert bottom blast. For best results, an ore should be used which contains more than 60% MnO_2 since with such ore a high reaction temperature will be achieved. The secondary slag which is formed in this second step, i.e., after withdrawal of the first formed slag and after introduction of additional manganese ore, contains considerably more manganese than the first formed slag. The manganese content of the second slag will be between 20 and 50%. If a sufficiently large converter is used, i.e., under favorable heat conditions, the steps of withdrawing slag and adding ore and burnt lime may be repeated at least once more.

To reduce manganese ores in a converter without supplying heat is considerably more difficult than to reduce iron ore, due to the difference in the thermodynamic conditions.

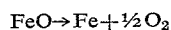
The free enthalpy of the reaction



equals:

$$G_{1600^\circ} = -58,500 \text{ cal.}$$

The corresponding figures for the reduction of iron are:



equals:

$$G_{1600^\circ} = -35,300 \text{ cal.}$$

Thus, it is much more difficult to reduce manganese than iron. In the case of reducing manganese oxide with a silicon-aluminum alloy this means that only within a defined narrow range will it be possible to obtain a metal of low silicon content while at the same time obtaining a slag of low manganese content and, furthermore, to carry out the process with a sufficient yield.

The amount of heat which is freed by reducing manganese ores with silicon-aluminum alloys is relatively very small.

The energy which is required for reducing oxides is characterized by the heat of formation of the oxides.

The heat of formation of MnO , $\Delta H_{298} = -92.5 \text{ kcal./mol.}$ while the corresponding figures for iron oxide are: $\Delta H_{298} = -64.5 \text{ kcal./mol.}$ This means that it is difficult to meet the heat requirements for the reduction of manganese ore with silicon-aluminum alloys without supplying outside heat.

According to the present invention, the heat balance is adjusted by using manganese ores which contain MnO_2 and MnO in definite proportions, whereby the ratio $\text{MnO}_2:\text{MnO}$ must be greater than 1.1:1. When complying with this condition, the heat which is freed by reduction of the manganese ore will suffice to heat the entire converter contents, to cause liquefaction and to reach a temperature favorable for carrying out the entire reaction. The optimum ratio MnO_2/MnO is between 1.25 and 2.5, since within this range it is possible, on the one hand, to use a reducing alloy of relatively low aluminum content while, on the other hand, the reaction will not proceed too violently and thus will not cause excessive smoke formation.

The manganese ores may also contain zinc and arsenic since these elements will be volatilized to a sufficient degree. Finally, it is possible to use finely subdivided ores without first agglomerating the same.

The method of the present invention is preferably carried out in a converter similar to a Thomas converter, however, with only a few tuyeres of less than 5 mm. diameter in the bottom of the converter.

For economical operation it is important that the lin-

4

ing of the converter will be of sufficient durability. Preferably the converter is lined with dolomite. In order to give the dolomite lining sufficient durability, it is necessary that the slag will be so composed as to be in the vicinity of the point of lime saturation, i.e., in the vicinity of the point of saturation of dicalcium silicate.

The relationships in the ternary system



are diagrammatically illustrated in the accompanying drawing.

Referring now to the drawing, it will be seen that the line indicating saturation of dicalcium silicate will bend at higher Al_2O_3 contents towards higher CaO contents. This means that higher Al_2O_3 contents will require an increase in the addition of lime. This, however, is not possible for reasons of the thermal conditions. Consequently, the Al_2O_3 content of the slag is limited to 22%. This corresponds to a ratio of Si/Al in the reducing alloy which must be greater than 1. The MnO content of the slag amounts at most to 17% and is not substantially affected by the ternary system. Thus, in a tetradic or quaternary representation, wherein the corners represent $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{MnO}$, the slag must be located within a space adjacent to the area indicated in the figure as ABCD, close to lime saturation at 1600° C. and reaching up to 17% MnO .

Keeping the foregoing in mind, the method according to the present invention will be described in more detail in the following example, without, however, limiting the invention to the specific details of the example.

Example I

The initial manganese ore had the following composition:

	Percent
MnO_2 -----	77.7
MnO -----	3.6
FeO -----	0.13
Fe_2O_3 -----	2.3
SiO_2 -----	7.7
Al_2O_3 -----	1.6
CaO -----	1.8
S -----	0.02
P -----	0.05
Ignition loss -----	10.2

After roasting at about 800° C. , the composition of the ore was as follows:

	Percent
MnO_2 -----	39.6
MnO -----	47.0
FeO -----	0.19
Fe_2O_3 -----	1.57
SiO_2 -----	7.1
Al_2O_3 -----	1.1
CaO -----	2.0
S -----	0.04
P -----	0.06
Ignition loss -----	1.1

Roasted and unroasted ore were mixed in the ratio of 3:1 so that the mixture contained 1.4 parts MnO_2 for each part MnO .

It also would have been possible to carry out the process with the initial unroasted manganese ore alone. However, by roasting part of the ore it was possible to save on reducing alloy. The presence of arsenic and/or zinc in the ore would not have interfered with the processing thereof. The ore was finely subdivided, having a particle size of less than 5 mm., and thus required no further comminution. Coarser ores are preferably comminuted to about 5 mm. particle size. It also would have been possible to form a mixture of roasted and unroasted ore wherein 1.25 parts of MnO_2 would have been present for each part of MnO , and by using a reducing alloy of

higher aluminum content, the proportion of MnO_2 could have been further reduced to 1.1 parts of MnO_2 for each part of MnO .

The above described ore mixture was reduced with an aluminum-silicon alloy of the following composition:

	Percent
Si -----	55.0
Al -----	29.5
Fe -----	10.8
Mn -----	0.1
C -----	1.3
P -----	0.04
N -----	0.1
Impurities -----	Balance

It also would have been possible to change the alloy composition providing that the combined percentage of aluminum and silicon would have remained between 65 and 90%, the balance being iron, manganese, titanium, carbon, calcium and about 2% impurities such as nitrogen, oxygen and phosphorus, and further provided that the percentage of silicon remained greater than that of aluminum. Optimum reaction speed would have been achieved with an alloy containing between 45 and 55% silicon and between 20 and 30% aluminum. A carbon content of less than 0.8% would have been more favorable for obtaining ferromanganese of very low carbon content.

The proportions of ore and reducing alloy which are to be mixed are calculated so that the oxygen equivalent of the ore based on the MnO_2 , MnO , FeO and Fe_2O_3 content thereof is determined as well as the oxygen equivalent of the alloy based on its reducing constituents, primarily Si, Al, Ti and C. The proportion of reducing alloy (A in percent) in an equivalent mixture is then calculated according to the formula:

$$A = \frac{E}{M+E} \times 100 (\%)$$

wherein E represents the oxygen equivalent of the ore and M the oxygen equivalent of the alloy. When it is desired to have in the mixture an excess of ore oxygen or of reducing alloy, the percentage of reducing alloy (C in percent) in the mixture will be calculated in accordance with the following formula:

$$C = \frac{100 \times (A - y)}{A \times \left(1 - \frac{y}{100}\right)} (\%)$$

wherein y indicates in percent the desired excess of oxygen. If $y < 0$ we have excess in reducing alloy.

According to the present example, ore and alloy were mixed in such proportions that the excess of ore oxygen equalled 0%, ($y=0$) in other words the oxygen of the ore was just sufficient for oxidizing the reducing alloy.

76.9 kg. of the mixture of roasted and unroasted ore described further above were mixed with 23.1 kg. of the reducing alloy.

In order to have available and to obtain in the slag the desired lime content, 48 kg. of burnt lime were added by introducing 20 kg. into the converter prior to further charging the same and pre-heating these 20 kg. to about 1200°C ., and by incorporating 28 kg. of burnt lime into the mixture of ore and reducing alloy, in order to achieve better dissolution of the lime and to prevent contact between highly acidic slag and the dolomite lining. It is also possible to control the speed of the deflagration by mixing lime with the ore-alloy mixture. At lower reaction temperatures a somewhat lesser addition of lime would have sufficed and at higher temperatures the proportion of lime could have been increased up to 60% of the weight of the ore-alloy mixture.

The mixture was then charged into the converter, ignited by priming in conventional manner and allowed to deflagrate with the converter in horizontal position.

After liquefaction, the converter was raised to upright position and simultaneously hydrogen gas was blown at an absolute pressure of 45 lbs. through the tuyeres in the bottom of the converter for a period of 2 minutes. Hydrogen gas consumption per thousand kg. of ferromanganese will amount to between 5 and 15 cubic meters of hydrogen gas of atmospheric pressure at ambient temperature. The gas pressure could also be reduced to about 22 lbs. Since the mechanical stirring effect is reached with little gas consumption a slight degree of oxidation would not unduly interfere with the process, only diminish the ferromanganese output by a little degree, it also would have been possible to blow with oxidizing gas as air carbondioxide, or a steam and oxygen, or mixtures of them.

The thus produced ferromanganese was of the following composition:

	Percent
C -----	0.48
Si -----	4.4
Mn -----	86.8
P -----	0.125
S -----	0.01
Fe -----	8.1

The slag was composed of:

	Percent
SiO_2 -----	31.3
Al_2O_3 -----	15.5
MnO -----	7.9
CaO -----	42.6
Fe -----	0.2
TiO_2 aso. -----	Balance

If the ore-alloy mixture would have been so proportioned as to contain an amount of ore oxygen greater than the amount required for oxidizing the reducing alloy, then the slag would have contained more manganese and the ferromanganese less silicon. The yield also would have been impaired.

The slag was then decanted and a mixture of 10.5 kg. of the initial unroasted ore and of 2 kg. burnt lime were additionally charged into the converter. In a larger converter with more advantageous thermal conditions, a greater amount of lime would have been added so as to again obtain a lime-saturated slag. It also would have been possible in a larger converter to additionally charge an ore with lesser MnO_2 content. In the present case, the excess of the ore oxygen over the amount required for oxidizing the entire silicon of the metal bath amounted to 45%. Depending on the desired final silicon content, such excess oxygen could have amounted to between 30 and 70%. The mixture in the converter was then stirred again for $1\frac{1}{2}$ minutes by blowing hydrogen into the same, and thereafter slag and metal were separately poured from the converter.

The thus obtained ferromanganese had the following composition:

	Percent
C -----	0.48
Si -----	0.80
Mn -----	87.9
P -----	0.124
S -----	0.01
Fe -----	10.3

The secondary slag had the following composition:

	Percent
SiO_2 -----	29.5
Al_2O_3 -----	6.3
Fe -----	0.38
MnO -----	37.8
CaO -----	29.9

The total amount of secondary slag is small and gets relatively smaller as the weight of the charge grows. It can be ground and added to the ore.

The yield of manganese amounted to 70%.

The ore which is additionally introduced for reduction of the silicon content of the ferromanganese preferably, for thermic reasons, should contain more than 60% MnO_2 .

The advantages of the present method include the following:

(1) The reaction is completed in a very short time, for instance, the batch produced in accordance with Example I was completed in 10 minutes.

(2) It is possible to produce ferromanganese of low carbon content and exactly the desired composition. For instance, in a steel mill, a small converter for the production of ferromanganese may be charged with solid materials and the produced molten ferromanganese may immediately be subjected to further processing without first being solidified.

(3) A great variety of manganese ores may be used as starting material due to the fact that mixing of ores, and of ores and reducing alloy, permits adjustments and corrections. Thus, with respect to the presence of arsenic and zinc as well as with respect to the MnO_2 content many different ores are suitable for the process of the present invention and, furthermore, finely subdivided ores may be processed without requiring an agglomerating treatment.

(4) There is no danger of freezing up of the converter.

It is also possible to utilize the present method for the refining of alloys containing up to 75% manganese, the balance usually consisting essentially of silicon, aluminum, iron and impurities. Such alloys are introduced in molten state as reducing alloys and the silicon content of such alloy must be greater than its aluminum content since the requirements with respect to slag formation are the same as discussed further above with respect to other reducing alloys. Should such alloy contain more aluminum than silicon, then an adjustment must be made by adding an appropriate amount of another alloy of relatively high silicon content. Due to the better thermic conditions which prevail when the alloy is introduced in liquid form, there is no definite upper limit of the Si/Al ratio. Preferably, an alloy is used containing between 60 and 70% manganese, between 20 and 30% silicon and up to 15% aluminum since the heat developed by the reaction of such alloy is just sufficient to assure a smooth reaction. With respect to the manganese ore which is to be reacted with such manganese-containing reducing alloy, the same conditions have to be met as were described further above with respect to other reducing alloys and completely solid charges. In all other respects the process is carried out as described further above, however, preferably with an addition of burnt lime equal to between 30 and 50% of the weight of the manganese ore.

Thus, according to the present invention as described above, ferromanganese containing more than 70% manganese, between 0.06 and 1% carbon and between 1.5 and 10% silicon is produced by metallothermic reaction.

Extensive experiments have shown that by proceeding in accordance with the present invention as described above, using a reducing alloy containing 1.3% carbon, careful operation will result in a ferromanganese containing 0.48% carbon. When it is desired further to reduce the carbon content of the ferromanganese, reducing alloys of lesser carbon content such as 0.8% carbon have to be used.

According to a further embodiment of the present invention, it is possible to produce ferromanganese of very low carbon content without having to work in the very careful and relatively expensive manner required when ferromanganese of very low carbon content is to be produced in the manner described above.

It is thus a further object of the present invention to provide, in accordance with a preferred embodiment of the above described method, a process which will result in ferromanganese of very low carbon content even if

reducing alloys of somewhat higher carbon content are used. This preferred embodiment of the present invention is of considerable importance in view of the great need for ferromanganese of lowest possible carbon content.

Surprisingly it has been found that a ferromanganese of very low carbon content may be produced by reacting the mixture of manganese ores with reducing alloy and burnt lime in the presence of an amount of sulfur equal to between about 0.8 and 4% of the weight of the manganese ore. Such addition of sulfur causes a marked reduction of the carbon content of the ferromanganese as will be described further below.

Although a full explanation of this phenomenon cannot be given, and without limiting the invention to any specific explanation of the manner in which the sulfur addition contributes to the reduction of the carbon content of the ferromanganese, probably the gases which are formed upon combustion of the sulfur to SO_2 will cause immediate thorough mixing of the bath constituents while the bath is being formed in the converter, so that more intimate contact is established between carbon and manganese oxides, resulting in the oxidation of such carbon to carbon monoxide. However, it is also possible that the sulfur at first is vaporized and thereby exerts its first stirring action which is augmented by a second stirring action upon oxidation of the sulfur to SO_2 .

According to the presently described embodiment of the present invention, it is again important to adjust the ratio MnO_2/MnO in the ore mixture so as not to include too much MnO which would make igniting of the mixture difficult, and also so as not to include too much MnO_2 in order to avoid excessive losses of manganese. Generally, however, and keeping the foregoing in mind, it is of course desirable to use an ore mixture of relatively high MnO content since this will reduce the proportion of reducing alloy required for carrying out the process.

When including sulfur in the reaction, preferably between 1.3 and 2 parts by weight of MnO_2 should be present for each part of MnO. Here again, the manganese ores are so chosen or mixed or roasted and mixed that the desired MnO_2/MnO ratio of the charge will be maintained. Thus, for instance, part of the ore may be completely roasted and then mixed with unroasted ore, or the entire ore may be partially roasted to the desired MnO_2/MnO ratio.

The required amount of reducing alloy will again depend on the oxygen content of the ore, however, when including sulfur in the process, the oxygen content should be more closely equal to the amount of oxygen required for oxidizing the reducing alloy, preferably the oxygen content of the ore will be equal to between 95 and 105% of the amount required for oxidizing the reducing alloy, and most preferably the oxygen content of the ore will correspond to the stoichiometric amount required for oxidizing the reducing alloy.

The Si/Al ratio of the reducing alloy preferably will be maintained between 1.5 and 3 if, in accordance with the presently described embodiment of the invention, sulfur is introduced into the converter.

The sulfur may be supplied in different ways. It is possible to use manganese ores which contain the required proportion of sulfur, however such ores are only rarely available. In most cases either sulfur or a suitable sulfide will be added, such as FeS or MnS, i.e., the pyrites or blends of iron and manganese. Preferably between 0.8 and 1.5% of FeS or between 0.8 and 4% of MnS, based on the weight of the manganese ore, may be added, whereby a larger proportion of MnS may be used since the manganese of the MnS will serve to increase the manganese content of the ferromanganese. However, it is also possible to use synthetically produced MnS or FeS. It is also possible to introduce finely subdivided sulfur such as sublimed sulfur in a quantity equal

to between 0.8 and 3% of the weight of the manganese ore.

Apart from the addition of sulfur or sulfides, the presently described embodiment of the invention does not differ substantially from the previously described embodiments. At first a fraction of the required burnt lime is introduced into the pre-heated converter which is formed with a basic lining and tuyeres or nozzles in its bottom. Thereafter the mixture of ore, sulfur or sulfide, and reducing alloy is introduced, and the mixture—unless it ignites by itself—is ignited by conventional priming. The contents of the converter will quickly liquefy. A preferably inert gas, i.e., a gas which will not react with the contents of the converter, such as hydrogen gas, is then introduced in order to achieve thorough stirring of the converter contents, then the slag is poured off and thereafter the ferromanganese may be tapped.

If during the reaction the contents of the converter have been heated to a sufficiently high temperature, it is possible after pouring of the first slag to introduce additional quantities of manganese ore and burnt lime in order to further reduce the silicon content of the ferromanganese. However, it is also possible to introduce oxygen through a lance into the bath in order to heat the same, and to add manganese ore and burnt lime separately, or to blow the additional quantities of manganese ore and burnt lime into the bath together with the oxygen.

The following example will serve to describe the method of the present invention including the addition of sulfur, without, however, limiting the invention to the specific details of the example.

Example II

The available manganese ore was of the following composition:

	Dried, Percent	Roasted, Percent
Fe	3.65	3.90
FeO	0.13	
Fe ₂ O ₃	5.08	
Mn	46.75	
MnO	4.19	47.00
MnO ₂	68.86	28.20
SiO ₂	7.46	
Al ₂ O ₃	6.96	
TiO ₂	0.59	
CaO	0.60	
MgO	0.22	
P	0.125	
S	0.01	
C	0.23	
Cu	0.07	
Ni	0.26	

The composition of the reducing alloy was as follows:

	Percent
Si	45.5
Al	30.6
Fe	19.1
Ti	1.84
P	0.034
S	0.02
C	1.27
Mn	0.23
Ca	0.91

In three different experiments the sulfur was added either as FeS of the following composition:

	Percent
Fe	63.26
S	31.51
C	0.19
Mn	0.17

or as sublimed sulfur.

In all three experiments a mixture of 30 kg. of dry ore and 39 kg. of roasted ore was used so that the ratio MnO₂:MnO equalled 1.62. Burnt lime was added in an amount equal to 48% of the ore. 21 kg. of the above de-

scribed reducing alloy were used so that the oxygen of the ore mixture corresponded to the quantity stoichiometrically required for oxidizing the reducing alloy.

In Experiment I, 2.18 kg. of the above analyzed iron sulfide were used; in Experiment II, 4.3 kg. of the same iron sulfide were added while in Experiment III the iron sulfide was replaced with 1.4 kg. of sublimed sulfur.

In each case hydrogen was introduced as bottom blast for stirring the bath in the converter.

The thus produced ferromanganese samples had the following compositions:

	Experiment I, Percent	Experiment II, Percent	Experiment III, Percent
C	0.45	0.44	0.38
Si	0.88	1.04	1.20
Mn	73.3	70.14	75.6
P	0.228	0.270	0.276
S	0.036	0.120	0.050
Fe	23.1	27.6	21.3

A fourth experiment was carried out exactly in the same manner as Experiments I-III, however, without adding sulfur in any form. The carbon content of the ferromanganese produced in Experiment IV was 0.60%. Thus, the experiments described in the present example clearly show that the addition of the relatively small percentage of sulfur or sulfide resulted in a marked reduction of the carbon content of the ferromanganese.

It appeared that the major portion of the added sulfur was oxidized and escaped as SO₂, since the slag contained only 0.384%, 0.776% and 1.14% sulfur, respectively, the highest sulfur content of the slag, i.e., 1.14% being found in Experiment II, i.e., in the experiment in which 4.3 kg. of the iron sulfide had been added.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of exothermically producing ferromanganese, comprising the steps of forming a mixture of manganese ore including as ingredients thereof MnO₂ and MnO, the ratio between MnO₂ and MnO in said manganese ore being greater than 1.1, a reducing alloy including silicon and aluminum in a combined amount of between 65% and 90% of said reducing alloy, the amount of aluminum in said reducing alloy constituting between one-half and one-fifth of the silicon present in said reducing alloy, said manganese ore and said reducing alloy being present in such proportions that the oxygen content of the ore is equal to between 90% and 110% of the amount of oxygen required for oxidation of said reducing alloy and an amount of sulfur equal to between 0.8% and 4% of the weight of said manganese ore; introducing the thus-formed mixture and an amount of burnt lime equal to between 40% and 60% of the weight of said mixture into a dolomite-lined converter; igniting said mixture so as to cause reaction of the same forming a liquid bath of silicon-containing ferromagnese and slag; blowing through said liquid bath a gas incapable of substantially oxidizing the same so as to intimately mix said ferromagnese and said slag; allowing the slag to separate from said liquid bath; and separately recovering said slag and said liquid bath from said converter.

2. A method of exothermically producing ferromanganese, comprising the steps of forming a mixture of manganese ore including as ingredients thereof MnO₂ and MnO, the ratio between MnO₂ and MnO in said manga-

11

nese ore being greater than 1.1, a reducing alloy including silicon and aluminum in a combined amount of between 65% and 90% of said reducing alloy, the amount of aluminum in said reducing alloy constituting between one-half and one-fifth of the silicon present in said reducing alloy, said manganese ore and said reducing alloy being present in such proportions that the oxygen content of the ore is equal to between 90% and 110% of the amount of oxygen required for oxidation of said reducing alloy and at least one sulfide in an amount corresponding to an amount of sulfur equal to between 0.8% and 1.5% of the weight of said manganese ore; introducing the thus-formed mixture and an amount of burnt lime equal to between 40% and 60% of the weight of said mixture into a dolomite-lined converter; igniting said mixture so as to cause reaction of the same forming a liquid bath of silicon-containing ferromanganese and slag; blowing through said liquid bath a gas incapable of substantially oxidizing the same so as to intimately mix said ferromanganese and said slag; allowing the slag to separate from said liquid bath; and separately recovering said slag and said liquid bath from said converter.

3. A method of exothermically producing ferromanganese, comprising the steps of forming a mixture of manganese ore including as ingredients thereof MnO_2 and MnO , the ratio between MnO_2 and MnO in said manganese ore being greater than 1.1, a reducing alloy including silicon and aluminum in a combined amount of between 65% and 90% of said reducing alloy, the amount of aluminum in said reducing alloy constituting between one-half and one-fifth of the silicon present in said re-

12

ducing alloy, said manganese ore and said reducing alloy being present in such proportions that the oxygen content of the ore is equal to between 90% and 110% of the amount of oxygen required for oxidation of said reducing alloy and an amount of sublimated sulfur equal to between 0.8% and 3% of the weight of said manganese ore; introducing the thus-formed mixture and an amount of burnt lime equal to between 40% and 60% of the weight of said mixture into a dolomite-lined converter; igniting said mixture so as to cause reaction of the same forming a liquid bath of silicon-containing ferromanganese and slag; blowing through said liquid bath a gas incapable of substantially oxidizing the same so as to intimately mix said ferromanganese and said slag; allowing the slag to separate from said liquid bath; and separately recovering said slag and said liquid bath from said converter.

References Cited in the file of this patent

UNITED STATES PATENTS

20	1,078,199	Heusler	Nov. 11, 1913
	1,363,657	Kalling et al.	Dec. 28, 1920
	2,369,112	Adeline	Feb. 6, 1945
	2,370,610	Adeline	Feb. 27, 1945
	2,549,994	Udy	Apr. 24, 1951
25	2,826,489	Wagner	Mar. 11, 1958
	2,830,890	Udy	Apr. 15, 1958
	2,830,891	Udy	Apr. 15, 1958
	3,000,725	Lofquist	Sept. 19, 1961

FOREIGN PATENTS

30	601,113	Great Britain	Apr. 28, 1948
----	---------	---------------	---------------