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PROCESS FOR THE MANUFACTURE OF MANGANESE OR OF MANGANESE ALLOYS POOR IN CARBON AND SILICON.

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To all whom it may concern:

Be it known that we, Bo MICHÄEL STURE KALLING and SVEN DAGOBERT DANIELI, subjects of the King of Sweden, residing at Trollhattan, in the Kingdom of Sweden, have invented new and useful Improvements in Processes for the Manufacture of Manganese or of Manganese Alloys Poor in Carbon and Silicon, of which the following is a specification.

The present invention relates to a process for the manufacture of manganese, or manganese alloys, poor in carbon and silicon, especially those with low percentages of phosphorus and iron, from manganese ores, whose principal content of manganese occurs in the form of oxides of manganese, in which the average degree of oxidation of the manganese is higher than is represented by the formula MnO, such for example as manganese ores which contain one or more of the minerals braunite, hausmannite, pyrolusite, polianite, psilomelan, or the like.

It is well known that manganese, or manganese alloys poor in carbon, can be manufactured in the following manner. Substances containing oxides of manganese, may be smelted with, or while in a molten condition brought into contact with silicon, or with alloys which contain silicon—preferably those containing more than 10% Si, as not until this percentage of silicon has been reached will the content of carbon have decreased sufficiently to be regarded as "low", for example ferro-silicon, ferro-silico-manganese, ferro-silico-aluminium-manganese, etc.

In order that this method may be usable for the manufacture of manganese alloys, it is indispensable that the reduction with silicon should take place under such conditions that neither the reagents nor the products formed by the reaction shall be capable of absorbing any appreciable quantity of carbon. For obtaining this result one may for instance use an electric furnace, the lining of which does not contain any carbon and in which the heat generation takes place in a free electric arc or arcs formed between two or several points of electrodes which are not in contact with the charge (for instance a furnace of the so called Rennerfelt-type). The chemical reactions which may take place in the process in question may be expressed schematically by the following formula:

$$Mn_aO_{(2d+1)} + Si_c = (MnO).(SiO_2)_d + Mn_{(a-1)}.Si_{(c-d)}.$$

The reaction does not proceed quantitatively, but ceases when the relation between the content of manganous oxide in the silicate slag formed, on the one hand, and the content of silicon in the manganese alloy formed, on the other hand, has reached a certain value, which value is a function of the content of silicon in the manganese alloy formed, and which relation increases according as the content of silicon in the alloy decreases.

In order that the content of silicon in the alloy obtained shall be low, it is essential that the content of manganous oxide in the silicate slag simultaneously formed, shall be high. Hence it is obvious that the consumption of silicon per unit of weight of reduced manganese will be higher, according as the degree of oxidation of manganese oxide to be reduced increases.

In order that the process of reduction in question may be carried out with the smallest possible consumption of silicon, and thus with the greatest possible economy, it is desirable that the degree of oxidation in the manganese of the manganese ore used shall be lowered as far as possible before the reduction with silicon is started.

It is conceivable that, inasmuch as it is well known that manganese oxides of a higher average degree of oxidation than MnO can be reduced to MnO with carbon monoxide or other reducing gases, a preparatory reduction of the ore with such gases might be practicable. However, in view of the practical difficulties of carrying out such a process on a large scale, this solution can scarcely be of any but academic interest.

In accordance with the present invention, the problem is solved in the following manner:—Manganese ore, whose content of manganese consists principally of manganese oxides with an average degree of oxidation above MnO, is smelted with a quantity of reducing carbon sufficient to bind the oxygen which the manganese oxides of the ore contain beyond the degree of oxidation MnO.

This reducing carbon is in addition to the quantity of reducing carbon that may be combusted with the carbon dioxide and water which may be given off by the ore during the smelting, and which quantity must be ascertained by experimental tests in each individual case. It has in fact been definitely ascertained, that no appreciable reduction of metallic manganese takes place until practically all the manganese in the ore has been reduced to the degree of oxidation which corresponds to the formula MnO.

It is obvious that by the present process a manganese ore admirably adapted for reduction with silicon will be obtained.

As a rule, manganese ores of the kind in question usually contain larger or smaller quantities of metal oxides, which are more easily reducible with carbon than is MnO, for example oxides of iron. In case it is desired that the alloy poor in carbon and silicon shall have the lowest possible content of metals whose oxides are more easily reducible than MnO, it is advisable to increase the quantity of reducing carbon supplied in the smelting process, so that the bulk of the said metal oxides shall be reduced to metal. Curiously enough, no appreciable quantity of manganese will follow along in the reduction.

Certain manganese ores of the kind in question, though otherwise good, contain appreciable quantities of phosphorus. When such ores are reduced with carbon to metal, practically the entire phosphorus content of the ore is obtained in the metal.

If it is desired that the manganese alloy poor in carbon and silicon shall be as far as possible free from phosphorus, it is possible, by equivalent increase of the admixture of carbon in the preparatory treatment of the ore with reducing carbon in accordance with the present process (in spite of the fact that phosphorus-pent oxide is more difficult to reduce than MnO) to have the phosphorus practically speaking, totally reduced, without entailing the reduction of any appreciable quantities of manganese, provided only that iron in sufficient quantities to bind the phosphorus so reduced is simultaneously reduced. Should the manganese ore which, in accordance with the present process, is to be treated with reducing carbon, contain too low a percentage of iron in proportion to that of phosphorus, it is advisable, in smelting the manganese ore with reducing carbon, to add a suitable quantity of oxides of iron, for example iron ore.

It is also evident from the above that manganese ores which, owing to too high a percentage of iron or too high a percentage of phosphorus, or both, are otherwise not adapted for the manufacture of manganese alloys, may be converted by the present process into ores admirably adapted for said purpose.

Having thus described the present process in so far as concerns the preparation of the manganese ore with a view to rendering it suitable for reduction with silicon, we shall proceed to explain how the reduction of the manganese oxide with silicon is performed in accordance with the present process.

It has been suggested that the substances containing manganese oxides (the manganese ores) should be supplied on the surface of a molten bath of silicon heated to a suitable temperature, for example in the form of silico-manganese or high-per cent ferro-silicon. In that case, however, the reaction between the silicon of the alloy rich in silicon and the oxides of manganese ore can take place only in the surface of contact between the alloy rich in silicon and the manganese ore, and therefore the reaction must proceed comparatively slowly, and its speed will necessarily be lowered according as the concentration of silicon in the alloy, or the concentration of manganese in the ore, is lowered. In accordance with the present invention, the mixing of the reagents is effected in the following manner: silicon, for example in the form of silico-manganese or high per cent ferro-silicon, is successively supplied in finely divided form on the surface of a molten bath of the ore previously treated with reducing carbon.

Every little grain of the silicon, or the alloy rich in silicon, is thus converted (as soon as the reaction between the silicon and the manganous oxide commences) into a little drop of silico-manganese alloy, the specific weight of which increases owing to the giving-off of silicon and the absorption of manganese, so that it becomes heavier than the molten manganese ore, and sinks down through the latter. The surface of contact between the drops of silico-manganese and the molten manganese ore is, of course, comparatively large, and, if the concentration of manganous oxide in the molten ore is sufficiently high, and the path which the drop of silico-manganese has to traverse in its downward progress through the ore is sufficiently long, practically all the silicon will have been oxidized during the fall of the drop, so that, manganese, or a manganese alloy poor in carbon and silicon will collect under the cover of molten manganese ore. This result, however, is subject to the condition that neither the reacting substances nor the reaction products are allowed during the process to absorb appreciable quantities of carbon.

Owing to the reaction of the metal drops with the molten manganese ore, the latter will be continuously deprived of manganous oxide and enriched with silicon dioxid, so that the concentration of manganous oxide

therein will eventually approach the limit when silicon is no longer oxidized to a satisfactory extent. The supply of silicon must then be discontinued and the furnace emptied, whereupon a new bath of manganese ore previously reduced by smelting with carbon should be prepared, and the supply of silicon can be recommenced.

As experience has shown that the molten manganese bath need not be very deep, the process can also be performed in the following manner. To a shallow manganese bath (which as a rule remains in the furnace when it is tapped off) is supplied a mixture of unmelted, previously reduced manganese ore, preferably in a finely pulverized state, and finely pulverized silicon, for example in the form of an alloy, a mixture so adjusted that the MnO concentration of the ore bath, owing to the successive supply of MnO entailed by the melting of the charge, and in spite of the successive absorption of silicon dioxide and reduction of manganese, is kept constant, until the furnace chamber is filled and must be emptied. This latter form of the process has the advantage that it is easier to protect the silicon of the alloy supplied against oxidation with free oxygen, and to prevent the caking of the small grains of the silicon alloy used for the reduction.

The actual performance of the process can, of course, be carried out in any furnace of suitable construction, but the process may most conveniently be performed in electric furnaces of a suitable type, and in one of the following ways: Either by using a single furnace in which a suitable quantity of manganese ore is first preparatorily reduced with carbon, whereupon the silicon is supplied on the surface of the bath of molten ore thus obtained, or else by preparatorily reducing the manganese ore with carbon in one furnace, and thereupon either discharging it in a molten condition direct into another furnace, in order there to be treated with silicon, or moulding it, after discharge, in suitable receptacles, where it is allowed to harden, in order to be transferred in a solid state—if desired, after grinding—to the second furnace, where the treatment with silicon is to take place.

A third combination, in which the same furnace is used alternately for the production of previously reduced manganese ore, which, after discharge, is allowed to harden, and for the reduction, with the aid of silicon, of preparatorily reduced ore, obviously coincides in principle with the latter of the above-mentioned alternatives.

It is obvious that, whichever alternative is selected, the lining of the furnace in which the reduction with silicon takes place, must not contain any appreciable quantity of carbon.

In the reaction between the preparatorily reduced manganese ore and the silicon, there is obtained, as above mentioned, a silicate slag which contains manganous oxide, and whose manganese content must be kept higher according as the silicon content in the manganese alloy poor in carbon is lower. It has, however, been found possible within certain limits to diminish the manganese content in this slag, provided the slag contains other bases. For example, it has been ascertained that two slags, one of which contained 70% MnO and 30% SiO_2 and the other 35% MnO and 30% CaO as well as 35% SiO_2, were in this respect equivalent.

The importance of this discovery lies principally in the fact that, per unit of weight of silicon consumed in the reduction, a smaller quantity of manganese in the form of slag, when lime (or other bases) is supplied to the process during the reduction with silicon is obtained, than when such bases are not supplied.

In the special case where a silico-manganese alloy is used as a reducing agent, it is possible to contrive that the slag precipitated as a by-product shall not contain a larger quantity of manganese than can be entirely utilized for the manufacture of the quantity of silico-manganese with which the reduction of the preparatorily reduced manganese ore is effected. In the production of silico-manganese alloy from such slag, one can as a rule count on an output of manganese of not less than 90%. This entails the advantage that the present process can be employed without the precipitation, as a by-product, of slag which requires to be used for the manufacture of other manganese alloys.

In the reduction with silicon (where lime has been added in the process) of the preparatorily reduced manganese ore, it has been found that if the lime has been insufficiently burned, or, if after the burning it has been allowed to lie for some time before use, part of the silicon supplied will be oxidized by oxidizing gases present in the lime, such as carbon dioxide and water.

It has been found possible to obviate this drawback by supplying lime (or other bases) to the manganese ore simultaneously with the smelting of the latter with carbon. It has in fact been found, curiously enough, that a slag which in the aggregate consists of MnO and CaO as to over 90%, is comparatively easily smelted, while at the same time it does not (in contra-distinction from high-basic calcium silicate slags) crumble into powder if kept for some length of time.

The fusibility is further increased by the presence of silicon dioxide, the content of which, however, need in no case exceed 15%. The fact that it has been possible to supply bases already in the first stage of the process also entails the advantage that limestone,

for example, can be used instead of lime, in conditions where electric power is cheap and the fuel required for the burning of lime is expensive.

In order to make clear the above statement, we give hereinbelow two series of chemical formulæ which schematically express the experience obtained in the manufacture of ferro-manganese poor in carbon and silicon, (A) with the use of the process which is the subject of the present invention, and (B) with previously known processes.

For the sake of completeness, the formulæ for the reactions which take place when the silicate slag, rich in manganous oxide, obtained as a by-product, is worked up into ferro-silico-manganese, are also appended.

A. Manufacture of ferro-manganese poor in carbon and silicon in accordance with the process which is the subject of the present invention:

1. Preparatory reduction of the manganese ore with carbon.

$$2(12Mn_2O_3 + Fe_2O_3 + 2SiO_2) + 2SiO_2 + 16CaO + 31C =$$

(manganese ore with circa 60% Mn, 5% Fe and 5.5% SiO_2) (quartz) (burnt lime) (reducing carbon)

$$47MnO.16CaO.FeO.6SiO_2 + Fe_3MnC + 30CO$$

(preparatorily reduced Mn ore with 55% MnO and 1.2% Fe) (Spiegel iron with 23% Mn) (escaping gases)

2. The reduction with silicon in the form of ferro-silico-manganese of the manganese ore preparatorily reduced with carbon with the addition of lime.

$$47MnO.16CaO.FeO.6SiO_2 + Si_{14}.Mn_{20}.Fe.C = 22MnO.16CaO.19SiO_2 + Mn_{45}.Fe_2.Si.C$$

(preparatorily reduced manganese ore) (silico-manganese alloy with 25% Si, 70% Mn, 0.8% C) (silicate slag with 33% Mn) (ferro-manganese with 94% Mn, 1% Si and 0.5% C.

3. The conversion of the silicate slag obtained as a by-product into silico-manganese alloy.

$$22MnO.16CaO.19SiO_2 + 4SiO_2 + FeO + 50C = 2MnO.16CaO.9SiO_2 + Si_{14}Mn_{20}FeC + 49CO$$

(silicate slag rich in manganese) (quartz) (oxide of iron belonging to quartz and reducing carbon) (reducing carbon) (waste slag with 7% Mn) (silico-manganese alloy) (escaping gases)

B. Manufacture of ferro-manganese poor in carbon and silicon in accordance with previous known processes:

1. Reduction of the manganese ore with silicon in the form of a silico-manganese alloy.

$$2.88(12Mn_2O_3 + Fe_2O_3 + 2SiO_2) + 1.89(Si_{14}.Mn_{20}.Fe.C) = 30.96Mn_2SiO_4 + Mn_{45}.Fe_{7.65}.C_{1.89}Si_{1.26}$$

(Mn-ore with circa 60% Mn, 5% Fe, 5.5% SiO_2) (silico-manganese alloy with 25% Si, 70% Mn and 0.8 carbon) (silicate slag with 55% Mn) (ferro-manganese with circa 83% Mn, 0.8% C and 1% Si)

2. Conversion of the silicate slag rich in manganese, obtained as a by-product, into silico-manganese alloy:

$$30.96Mn_2SiO_4 + 14.07SiO_2 + 2.81FeO + 157.6C =$$

(silicate slag with 55% Mn) (quartz) (oxide of iron accompanying quartz and reducing carbon) (reducing carbon)

$$(1.89 + 0.92)Si_{14}Mn_{20}.Fe.C + (154.79CO + 5.72Mn + 5.69Si).$$

(ferro-silico-manganese) (escaping gases)

On comparing the above formulæ it will be found that:

(*a*) In the present process about 52% of the manganese content of the ore supplied to the process is recovered in the manganese alloy poor in carbon, while in the previous process merely somewhat over 10% is obtained in the reduction with silicon.

(*b*) Per unit of weight of manganese obtained in the form of a manganese alloy poor in carbon, the consumption of reducing silicon is about 90% higher in the latter than in the former case.

(*c*) The consumption of ore per unit of weight of manganese obtained in the form of manganese alloy poor in carbon is in the latter case about 44% higher than in the former.

(*d*) The manganese content in the alloy poor in carbon obtained is about 10% higher in the former than in the latter case.

(*e*) The content of carbon in the former case is scarcely more than half as large as in the latter.

(*f*) In the latter case the silicate slag rich in manganese, obtained as a by-product, contains so large a quantity of manganese that it cannot be fully utilized for the manufac-

ture of the equivalent quantity of silico-manganese alloy with which the reduction took place, whence it follows that, when the earlier process is adopted, the manufacture, in order to yield the best possible economic results, must be combined with the manufacture of, for example, ordinary ferro-manganese rich in carbon, or silico-manganese alloys. It should be observed that a manufacturing process which in order to pay, has to be combined with another kind of manufacture, as a rule, diminishes the value of the process.

It is to be understood that wherever we have used the expression "manganese" in the specification and claims, this expression is intended to cover not only manganese as such, but also alloys thereof, and where we have used the expression "manganese alloy" it is intended to cover not only an alloy of manganese, but manganese as metal.

Having thus described our invention we declare that what we claim is:

1. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace with a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

2. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace with a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, said silicon being supplied in a finely pulverized state on the surface of a molten bath of prereduced manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

3. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace with a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, the silicon being supplied in a finely pulverized state and mixed with pulverized prereduced manganese ore on the surface of a molten bath of prereduced manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

4. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace with a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, said silicon being supplied in a finely pulverized state and mixed with pulverized prereduced manganese ore and basic substances such as lime on the surface of a molten bath of prereduced manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

5. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese

oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace together with lime and a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys, preferably having more than 10% of silicon, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

6. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of manganese higher than is represented by the formula MnO in an electric furnace together with lime and a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, said silicon being supplied in a finely pulverized state on the surface of a molten bath of prereduced manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

7. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace together with lime and a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, said silicon being supplied on the surface of the molten bath of prereduced manganese ore in a finely pulverized state and mixed with pulverized manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

8. The process of manufacturing manganese poor in carbon and silicon, and having low percentages of phosphorus and iron, which consists in smelting manganese ores in which the principal content of manganese occurs in the form of manganese oxides having an average degree of oxidation of the manganese higher than is represented by the formula MnO in an electric furnace together with lime and a quantity of reduction-carbon adapted to reduce the main part of the higher manganese oxides of the ore into manganous oxide, a part of the eventually occurring iron oxides to iron and a part of the eventually occurring phosphoric combinations to phosphorus, then reducing the prereduced manganese ore in an electric furnace by silicon in the form of alloys preferably having more than 10% of silicon, said silicon being supplied on the surface of the molten bath of prereduced manganese ore in a finely pulverized state and mixed with pulverized manganese ore and basic substances such as lime, on the surface of the molten bath of prereduced manganese ore, the latter reduction taking place under such conditions that the metal formed has no opportunity to absorb any appreciable quantity of carbon.

In testimony whereof we have signed our names to this specification.

BO MICHAEL STURE KALLING.
SVEN DAGOBERT DANIELI.

Witnesses:
AUG. HAGELIN,
E. NILON.