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PROCESS FOR PRODUCING METALS AND ALLOYS.

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To all whom it may concern:

Be it known that we, SVEN DAGOBERT DANIELI and BO MICHAËL STURE KALLING, subjects of the King of Sweden, and residing in Trollhattan, in the Kingdom of Sweden, have invented certain new and useful Improvements in Processes for Producing Metals and Alloys; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to an improved process for the production, by silico-thermic reduction, of metals and alloys poor in carbon and silicon. More especially it is intended for the production of metals and alloys practically free from carbon (i. e. with less than 0.25% C.) and poor in silicon, such as, for example, a ferro-chromium alloy or a ferro-manganese alloy.

When a substance containing oxygen compounds, such for example, as an ore containing metallic oxides, is reduced with silicon, for example in the form of a high-silicon alloy with more than 10% of silicon, a low-carbon metal or low-carbon alloy as well as a silicate slag are, obtained, if the reduction is carried out under such well known conditions that no carbon is supplied from outside during the process. If the metal or alloy reduced is moreover to be poor in silicon, the oxidizing agent must be supplied in excess, resulting in the formation of a slag as a by-product rich in metal oxides, the content of the latter being high when the silicon content of the metal or alloy produced is low, and vice versa.

If it is desired that the metal or alloy reduced by the silico-thermic process should be practically free from carbon, the reducing agent employed must consist of silicon or a silicon alloy with a silicon content which should not be lower than 40%, but may be higher, for example 50% or more.

The quantity of slag formed in the reduction, particularly if pure silicon or an alloy with at least 40% of silicon is employed, will be comparatively large, if the metal or alloy produced is to be poor in silicon. The slag produced, as a general rule, can be utilized only in part as raw material in the manufacture of a silicon alloy comparatively rich in silicon, for example a silicon alloy with up to about 40% Si. That this is really the case is clearly illustrated by the following reaction representing as nearly as possible actual conditions of practice. In this reaction Me designates a metal the atomic weight of which is lower than 56, for example Cr or Mn.

$$6Me_2O_3+3MeSi_2+8CaO=(\text{metal oxide})+(\text{alloy with more than 40\% Si})+(\text{flux})=9Me+2(3MeO.4CaO.3SiO_2)$$ (metal practically free from carbon and poor in silicon) + (silicate slag, rich in metal oxide).

The above reaction shows with sufficient clearness that the slag formed as a by-product contains twice as much metal as the quantity supplied to the reduction process in the form of a silicide.

This defect in the silico-thermic reduction process of yielding as a by-product a quantity of slag rich in metals which cannot be completely utilized with advantage is eliminated by our present process of producing low-carbon and low-silicon metals and alloys by the silico-thermic reduction of ores. The characteristic and essential feature of the process is that the reducing agent consisting of silicon or silicon alloys relatively rich in silicon, preferably with at least 40% of silicon, is first oxidized with an insufficient quantity of oxidizing agent, such as an ore containing metallic oxides, for forming an alloy poor in carbon and relatively rich in silicon (but in all cases with a percentage of silicon lower than that in the alloy which has been partially oxidized) and a silicate slag which is relatively poor in metal oxides. It will be understood that when the silicate slag is poor in metal oxides, the silicon content of the metals or alloys formed generally will be high. The last-mentioned alloy relatively rich in silicon is then oxidized with an "excess" of ore, which results in the formation of a slag rich in metal oxide, and a metal or alloy low in carbon and silicon. This slag, other circumstances being equal, is richer in metal oxide according as the low-carbon metal or alloy is lower in silicon.

The essential advantage of our process, as compared with the older process described above should be sufficiently clear

from the following respresentative reactions, in which Me signifies the same as above:

Reaction Ia:

$3Me_2O_3+Me_3Si_7+4CaO=$(metal oxide in insufficient quantity)+(metal silicide rich in silicon)+(flux)$=Me_8Si_3+MeO.4CaO.4SiO_2$ (metal silicide for reaction Ib, see below)+(silicate slag poor in metal oxide).

Reaction Ib:

$Me_8Si_3+3Me_2O_3+4CaO=$(metal silicide from reaction Ia)+(metal oxide in "excess")+(flux)$=11Me+3MeO.4Ca_2O.3SiO_2$(low-carbon and low-silicon metal)+(silicate slag rich in metal oxide).

It should be evident from the last two reactions that the metal oxide contained in the silicate slag rich in metal oxide formed in accordance with reaction Ib yields a quantity of metal equivalent to the metal content of the silicide supplied in accordance with reaction Ia, which means that the slag formed can be completely utilized for the production of a quantity of silicon alloy necessary for the process in its entirety.

The following reactions show another application, valuable under certain conditions, of our process:—

Reaction IIa:

$3MeO.4CaO.3SiO_2+MeSi_4=$(slag rich in metal oxide from reaction IIb in insufficient quantity (see below)+(metal silicide rich in silicon).

$3MeSi+MeO.4CaO.4SiO_2$ (metal silicide for reaction IIb)+(silicate slag poor in metal oxide).

Reaction IIb:

$3Me_2O_3+3MeSi+4CaO=$(metal oxide in excess)+(metal silicide from reaction IIa)+(flux)$=6Me+3MeO.4CaO.3SiO_2$ (low-silicon metal practically free from carbon)+(silicate slag rich in metal oxide used in reaction IIa).

Reaction IIa+IIb:

$3Me_2O_3+MeSi_4+4CaO=6Me+MeO.4CaO.4SiO_2$ (metal oxide)+(metal silicide rich in silicon)+(flux)=(low-silicon metal practically free from carbon)+(silicate slag poor in metal oxide).

It will be easily understood from the last group of formulae that our process can be applied in such a way that no slag rich in metal oxide need be obtained as a by-product. It ought to be obvious that in the above representative reactions pure metal oxide has been chosen as example instead of "ore". In principle there is no difference if the ore, in addition to one or more metal oxides reducible with silicon, should contain also other substances, such as for example MgO, Al_2O_3, SiO_2, and so forth.

In the reactions Ia, Ib, IIa and IIb, a silicon alloy of the same metal as that to be reduced from the ore is given as an example of a reducing agent. Naturally there will be no essential change if a silicon alloy of a metal other than that or those occurring in the ore is employed as a reducing agent. In the latter case the product will merely be an alloy instead of an unalloyed metal. It should be evident from reaction IIa that it is possible to start from pure silicon instead of from a silicon alloy rich in silicon. Likewise it will be apparent from the same reaction that in the case of the silico-thermic production of very costly metals or alloys, it is possible to utilize completely even the slag relatively poor in metal oxide as raw material for the production of a reduction alloy.

Finally it should be mentioned in this connection that when in the above we speak of "ore" in insufficient quantity or "ore" in "excess", we mean that the content of oxygen in oxides supplied to the process and reducible with silicon is too small to be able to bind, or respectively too large to be entirely consumed in the binding of a quantity of silicon simultaneously supplied in the form of a silicon alloy.

The theoretic aspect of our process having thus been illustrated in detail by the above, we shall now, in order to elucidate it further, describe its practical application:—

Seeing that, as we know, the silico-thermic reduction in general proceeds endo-thermically, heat from outside must be supplied during the various stages of the process. The part or phase of the process in which an alloy relatively rich in silicon, for example with more than 40% of silicon, is partially oxidized (indicated by the reactions Ia and IIa), can be carried out in a Bessemer converter. In that case the necessary heat can be obtained by the process that part of the silicon supplied is combusted with free oxygen, e. g. in the form of air. This process is rapid and yields a slag practically free from metal oxide, but presupposes the condition that at least one of the necessary substances can be introduced into the converter in a molten state. Obviously the same phase of the process can be carried out in a suitable electric furnace, e. g. in a known manner. The part of the process which relates to the actual production of the metal or alloy poor in carbon and silicon is most advantageously carried out, in a suitable electric furnace. Bessemerizing with air for the carrying out of this latter stage entails difficulties in obtaining a final product sufficiently free from nitrogen.

By way of further elucidation, we shall

finally, as an example, describe the production, in accordance with one mode of our process, of low-silicon ferro-chromium practically free from carbon.

In a suitable electric furnace, e. g. a single-phase furnace in which the current is supplied both through an adjustable carbon electrode and through the furnace lining, a slag bath rich in chromium is produced, for example by the smelting of a suitable quantity of silicate slag, rich in chromium, from a previous process. The high chromium slag bath thus produced is supplied with a suitably proportioned quantity of ferro-silico-chromium with more than 40%, e. g. 45%, of silicon. The reaction between the substances supplied, provided that the proportions between them are properly proportioned, will yield firstly an alloy practically free from carbon with a lower silicon content than that in the alloy originally supplied, and secondly a slag practically free from chromium. The slag free from chromium is tapped off and discarded whilst the alloy free from carbon but relatively rich in silicon is transferred in a fluid or solid state to another similar electric furnace, in which in the meantime a molten chromium ore bath has been arranged. The reaction which takes place in this second furnace between the chromium ore bath and the silico-chromium alloy practically free from carbon supplied to it from the first furnace will yield, if the quantities are properly proportioned, a low-silicon ferro-chromium practically free from carbon and a high-chromium silicate slag, which latter is transferred in a solid or fluid form to the first mentioned furnace in order to be freed there, in the manner indicated above, from the main part of its chromium content, whilst the carbon-free ferro-chromium from the second furnace is removed thence and allowed to solidify, or is used in a molten form for a suitable purpose, e. g. in order to form, together with melted low-carbon iron material for the production of stainless steel or iron. By choosing proportions between the silicon content in the alloy supplied to the slag bath in the first furnace and in the alloy produced therein, it is possible to arrange that the high-chromium slag obtained in the second furnace can entirely be consumed in the first furnace, for the manufacture of the quantity of silico-chromium alloy which is successively consumed in the other furnace.

It should be evident that the mode of our process which has been exemplified above is also applicable to the silicothermic production of an alloy with a higher carbon content than 0.25%, in which case one can proceed from a ferro-silico-chromium alloy with less than 40% Si. It is also manifest that it is not essential to our process that two furnaces, or two groups of furnaces, should be used. It is possible also to use only one furnace, in which case one may proceed, for example, as follows:— When the high-chromium slag has been freed from the main part of its chromium content, it is removed in some suitable way, whereupon molten chromium ore is supplied to the silico-chromium alloy retained in the furnace, until that alloy has been sufficiently desilicized, which resuts in the formation of a high-chromium slag, which is retained in the furnace whilst the alloy is being removed, whereupon a fresh quantity of silico-chromium alloy is supplied by which the chromium slag bath is partly desilicized, and so forth.

It is likewise evident that it is possible in a single furnace to perform one stage or phase of the process for some length of time, in order afterwards to use the furnace for some length of time for the performance of the other part of the process.

Finally it should be mentioned that our process is also direct applicable for the manufacture of ferro-chromium poor in carbon and silicon and with a relatively low content of chromium, e. g. 8–30% Cr, an alloy from which stainless articles can be manufactured by a suitable process. In order to attain this object, it is obviously merely necessary to modify the above described production of ferro-chromium (which as a rule means an alloy with 60 to 70% Cr) by supplying a suitable quantity of low-carbon iron in a solid or molten form at a suitable moment during the first or second phase of the process.

It should also be evident from the above that ferro-manganese low in carbon and silicon can be produced from manganese ore in a manner analogous to that described above.

"Percentage" (%) in this specification and in the claims always means percent by weight.

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

1. Process for the production of metals or alloys of low carbon and silicon content by silico-thermic reduction which comprises oxidizing an alloy having a relatively high silicon content with a metal oxide to produce a silicate slag relatively low in metallic oxides and a metallic silicide low in carbon and relatively high in silicon, thereafter treating said metallic silicide with a metallic oxide to produce a metal relatively low in carbon and silicon and a silicate slag relatively high in metallic oxide, and separating the metal thus formed.

2. Process for the production of metals or alloys of low carbon and silicon content by silico-thermic reduction which comprises oxidizing an alloy having a relatively high silicon content with a molten silicate slag rich

in metallic oxides to produce a silicate slag relatively poor in metallic oxide and a metallic silicide low in carbon and relatively high in silicon, thereafter treating said metallic silicide with a molten metallic oxide to produce a low carbon and low silicon metal and a silicate slag relatively high in metallic oxide, and separating the metal thus formed.

3. Process for the production of metals or alloys of low carbon and silicon content by silico-thermic reduction which comprises supplying a solid alloy having a relatively high silicon content to a molten silicate slag rich in metallic oxides to produce a silicate slag relatively low in metallic oxides and a metallic silicide low in carbon and relatively high in silicon, thereafter supplying the metallic silicide thus formed in solid form to a molten bath containing metallic oxides in an amount greater than the equivalent of the silicon content of the metallic silicide to produce a metal relatively low in carbon and silicon and a silicate slag relatively high in metallic oxides, and separating the metal thus formed.

4. Process for the production of metals or alloys of low carbon and silicon content by silico-thermic reduction which comprises oxidizing an alloy having a relatively high silicon content with a metal oxide to produce a silicate slag relatively low in metallic oxides and a metallic silicide low in carbon and relatively high in silicon, thereafter treating said metallic silicide with a metallic oxide to produce an alloy relatively low in carbon and silicon and a silicate slag relatively high in metallic oxide, and separating the alloy thus formed.

5. Process for the production of ferro-chromium alloys having a low carbon and low silicon content by silico-thermic reduction which comprises oxidizing an alloy having a relatively high silicon content with a silicate slag rich in chromium oxide to produce a low carbon silico-chromium alloy with a relatively high content of silicon and a silicate slag relatively poor in chromium oxide, supplying the silico-chromium alloy thus formed in solid form to a molten bath containing ferro-chrome ore having a content of chromium oxide in amount exceeding the equivalent of the silicon content of said silico-chromium alloy to produce a ferro-chromium alloy low in carbon and silicon and a silicate slag rich in chromium oxide, and separating the ferro-chromium alloy thus formed.

In testimony whereof we have hereunto set our hands this 17th day of November 1923.

SVEN DAGOBERT DANIELI.
BO MICHAËL STURE KALLING.

In presence of—
OSCAR SKARBERG,
OSCAR SWANBERG.