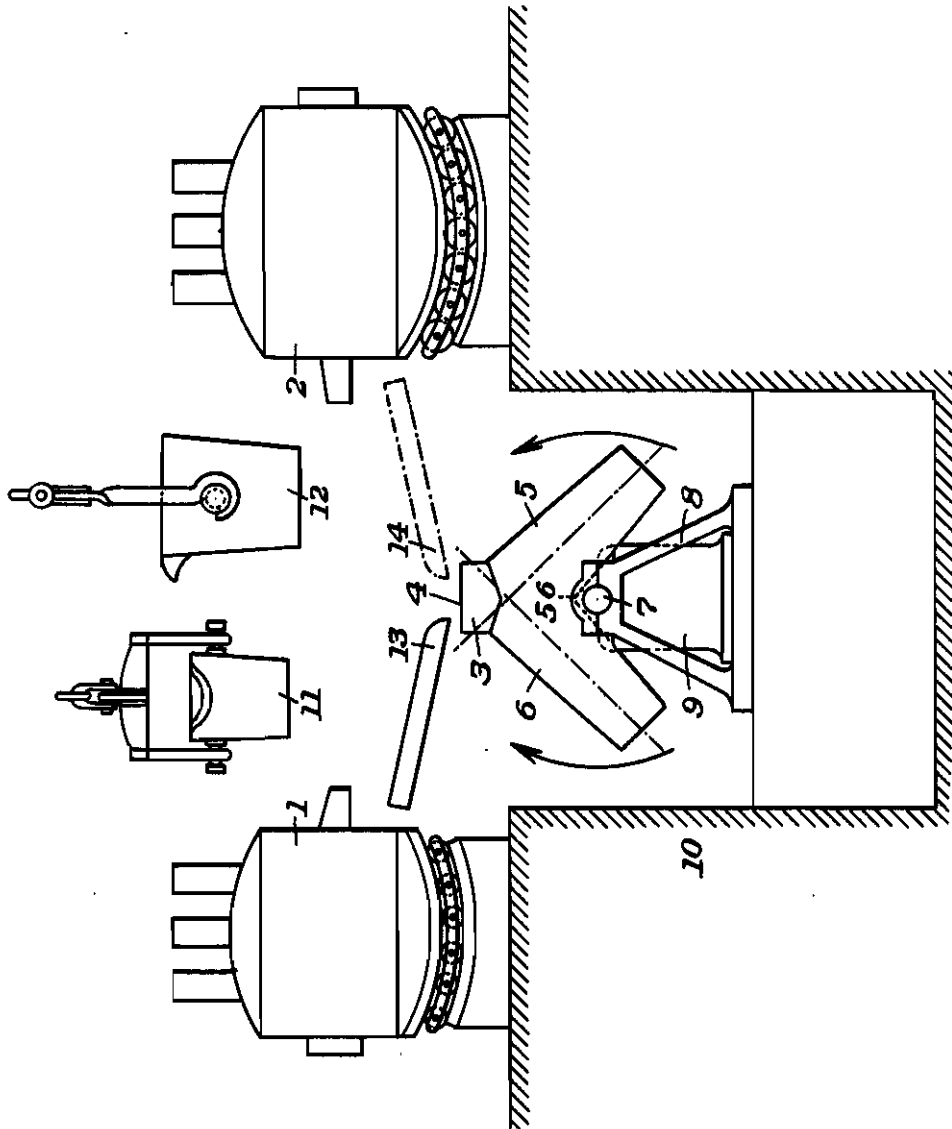


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MANUFACTURE OF LOW-CARBON FERRO-ALLOYS
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MANUFACTURE OF LOW-CARBON FERRO-ALLOYS

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It is known that the manufacture of low carbon ferro-alloys generally comprises two distinct principal steps. In the first step, an alloy rich in silicon, e. g. ferro-silicon, is manufactured, e. g. by reducing by means of carbon in an electric furnace, a suitable mixture of silica and of ore of the alloying element, an addition of lime being usually made in order to fluidify the slag which is formed during the process. The alloy obtained in this first step has a low carbon content. In the second step, the silicon-alloy which has been obtained during the first step, is treated by means of a slag which is rich in the oxide of the alloying element, in view of eliminating the silicon and finally obtaining a ferro-alloy which is at the same time poor in carbon and in silicon. The iron present in the said alloy is originated either from the ore which is heated in the electric furnace or from the oxide of the alloying element which may be mixed with an oxidic compound of iron, or again from both ore and oxide, or also from ferrous metal, e. g. mild steel scraps, added in the furnace.

In the previous processes, the second step of the operation was often carried on in a furnace and several slagging off operations were necessary, or an important amount of oxide of the alloying element was systematically left in the final slag. In all these processes the said operating steps led to bad yields in alloying element owing to the insufficient exhaustion of the slag as concerned the oxide of the said alloying element.

The process hereabove recalled has been largely used for the manufacture of ferro-chromium, the iron being contained both in chromium ore which is treated in the electric furnace, and in chromium oxide which was made a constituting part of the desiliconizing slag. Ilmenite was practically the material to which it was resorted in that case, as being the ore of the alloying element and also the oxide forming the basis of the desiliconizing slag. Both the chromium and the iron oxides were reduced by the silicon of the silicon-alloy and thus iron passed into the alloy.

More recently the applicant has proposed, in order to accelerate the second step and to increase the yield thereof, to energetically intermix the molten silicon-alloy and the slag, which rapidly realises a chemical equilibrium between slag and silicon-alloy. However, when in such a process an attempt has been made to lower to very small figures the silicon in the final alloy, it has proved that important quantities of oxide of the alloying element were necessarily left in the slag.

Although such quantities are much smaller than those resulting from a treatment which does not comprise an energetic intermixture of silico-alloy and desiliconizing slag, it is obvious that it would be much more advantageous to keep them down. As a matter of fact, when the said process is used for the manufacture of a ferro-chromium having a low content of silicon, it is necessary to leave in the final slag a chromium oxide (Cr_2O_3) content comprised between 4 and 8%. Accordingly, it is generally resorted in the processes hereabove recalled to a practice in which the desiliconizing slag which has been insufficiently exhausted as concerns the oxides, is charged anew in the furnace in which the silicon-alloy has been manufactured and where it is subjected again to a reducing operation. But this method of carrying out the process led to an increase in the net cost of the manufacture of the silicon-alloy.

The present invention refers to a process for the manufacture of low carbon ferro-alloys.

One object of the invention is to ensure a very economical run of the silicon-alloy furnace.

Another object of the invention is the obtention of a ferro-alloy which has a very low final content of silicon in the ferro-alloy, at a low cost and in a short time.

Another further object of the invention is to nearly totally exhaust the slag used for the desiliconizing, as concerns the metallic oxides contained therein.

Other further objects of the invention result of the disclosure set forth in the following part of the present specification and in the appended claims.

The process according to the invention consists in manufacturing a low carbon alloy which contains a high proportion of reducing agent, for instance silicon, by reducing by means of carbon preferably according to an acid run of the alloy-furnace, a mixture of an oxidic compound of the reducing element e. g. of quartz, and of an oxidic compound of the metal to be alloyed, for instance an oxide thereof, and then by successive operations, the content of silicon of the alloy thus obtained, by means of a slag which has as a basis an oxidic compound of the alloying metal and a non volatile base such as lime, namely: an operation comprising an energetic intermixing between the said alloy in molten state, and slag resulting from the second operation carried on on a preceding melt, intermixing by which the said slag is practically exhausted as concerns the oxidic compound of the alloying metal, and

by which the alloy rich in reducing agent is partially oxidized as concerns the said reducing element, and another operation comprising a treatment of the said partially oxidized alloy, by means of a fresh slag having as a basis an oxidic compound reducible by the reducing agent of the alloy, e. g. an oxide or ore of the metal to be alloyed and a non volatile base, such as lime, treatment by which the reducing agent of the alloy is oxidized down to the final content which is wanted as concerns the reducing agent.

The process according to the invention thus essentially comprises three stems, namely, first step, manufacture of a primary alloy rich in reducing agent and poor in carbon; second step, an oxidizing operation of the said alloy to transform it in an intermediate alloy having a medium content of reducing agent, and to give rise to an exhausted slag; third step, a second final oxidizing operation to transform the intermediate alloy into final low-reducing-agent alloy, and to give rise to an intermediate slag having a medium content of oxidizing substance which is used for treating a fresh batch of primary alloy as above set forth. This process ensures, owing to the combination of these three steps, the obtention of low carbon and even very low carbon ferro-alloys having a very low content of reducing agent with a total yield which is extremely high as concerns the alloying metal and at a net cost decidedly lower than the previously known processes.

The process according to the invention can be applied to the manufacture of any low carbon ferro-alloy: ferro-chromium, ferro-manganese, ferro-titanium, ferro-molybdenum etc. The reducing agent which is preferably used is silicon. However, in the following description and for the sake of simplification, it will be more specially referred to the manufacture of ferro-chromium, silicon being used as reducing agent, but it should be understood that the explanations given in the said disclosure apply as well, with the necessary modifications, to the manufacture of any other ferro-alloys coming in the range of the present manufacturing process and to any other chemically equivalent reducing agent.

In the manufacture of a ferro-chromium according to the process of the invention, the first step, consisting in the manufacturing of silico-chromium in a furnace, is notably characterised in that it practically necessitates but the handling of fresh materials, namely, chromium ore and silica—preferably quartz—without any use of used slags or any necessary addition of fluidifiers. The subsequent desiliconizing operations do not in fact finally give rise to any residue which is rich in chromium oxide which necessitates a further treatment in the silico-chromium furnace, because the slag which is used for these desiliconizing operations is finally practically exhausted as concerns the oxides, especially the oxide of the alloying metal. In the previous processes where the residual slag resulting of the desiliconizing operation were subjected to a further reducing operation in the silico-chromium furnace, the important proportion of lime contained in the slag led to an extra expense of thermal energy for melting again the slag and compelled to carry on a reduction operation at a relatively high temperature, owing to the enrichment in lime of the materials to be fused and to the lowering of the percentage of the content of free silica. Experience has shown that the reduction of the mixture of chromium ore and quartz takes

place in very favourable conditions when the run of the furnace has an acid character, according to the invention. The operation can further be carried on at a less elevated temperature for a same content of silicon in the silico-alloy, than with slags which are rich in lime, and without it being necessary to add fluidifiers. As a mere indication the consumption of electric current when manufacturing low carbon silico-chromium having a very low content of silicon according to the invention, is lowered by 20 to 30% when compared with the previous processes, which constitutes a considerable saving of money and increases the daily output of the furnace.

Moreover, the acid running of the silico-chromium furnace has the advantage that for an equal content of silicon, the silico-chromium obtained has a carbon content lower than the one which is obtained in the previous processes. This allows accordingly, either to manufacture silico-chromium and consequently ferro-chromium having a lower content of carbon, or the content of carbon being finally the same as before, to start from silico-chromium having a lower content of silicon, which constitutes a further saving of money owing to the amount of quartz to be used and to be fused being curtailed.

It should be however underlined that the acid run hereabove referred to for the manufacture of the silico-chromium is rendered economically possible only because the means which are provided by the invention for the desiliconizing of the silico-chromium lead to a nearly total exhaustion of the residual slag as concerns chromium oxide.

The second step of the process comprises a partial first desiliconizing operation of the silico-chromium which has been manufactured in the first step. This partial desiliconizing is carried on by means of desiliconizing slag resulting of the third step of a precedent melt, and which is already partially exhausted as concerns chromium-oxide but still contains important quantities of the latter. The treatment is advantageously carried on by energetically intermixing the silico-chromium and the slag, both in molten state, according to any of the known processes previously proposed by the inventor for intermixing metal and slag, namely intermixing by a rapid pouring of the molten metal in thick jet from a considerable height onto the molten slag placed in a ladle; or intermixing by means of an apparatus comprising two rocking or rotating receptacles closely opposed to each other by their openings, the content of one receptacle being violently poured in the second one and vice-versa; or again intermixing the metal and slag by repeatedly lifting these two substances and allowing them to simultaneously tumble down by successive rolling operations, in an apparatus formed of two frusto-conical chambers united by their largest sections and rotated about a transverse common axis, the speed of rotation of the apparatus being high enough that some interpenetration of the slag and metal contained therein takes place. Such intermixing leads according to the invention as it has been disclosed hereabove, to a nearly total exhaustion of the slag as concerns Cr_2O_3 and to a desiliconizing of the silico-chromium which is only partial.

At last, in the third step of the process, the silico-chromium, which has been partially desiliconized during the second step hereabove referred to (first desiliconizing operation) is taken again and treated by means of a slag having as

a basis chromium ore and lime. This treatment can be carried on by any convenient means, either by an intermixing of alloy and slag, which is always preferable, or without intermixing. The operation can notably be carried on in one of the apparatus hereabove referred to and by the processes described in connection therewith, or in any other intermixing apparatus, or also by violently pouring the metal onto the slag in a ladle, from a considerable height, or in a furnace by any known process, starting from silico-chromium, either in solid or in molten states, the slag being partially or totally charged in a molten state. The amount of chromium ore which has to be used is calculated in such a way that practically, the quantities of reducible oxides contained in the ore (Cr_2O_3 and FeO) stoichiometrically correspond to the total amount of silicon which has to be eliminated out of the silico-chromium alloy. As a rule, the higher is the proportion of lime, the lower is the final content in the silicon and the higher should be the content of Cr_2O_3 in the third step. The amount of lime to be added also depends upon the composition of the ore. The higher is the proportion of chromium oxide with respect to the iron oxide the greater should be the amount of lime added. The lime may be partially replaced by another basic substance or other substances such for example as magnesia.

During this last step, the desiliconizing of the silico-chromium can be carried on until the figure which is wanted is reached, the final content of silicon which is obtained being the lower the higher are the contents of the slag in basic substances and Cr_2O_3 . Owing to the fact that in this third step a relatively high content of the resulting slag can be reached as concerns Cr_2O_3 without inconvenience—the said slag being used again in the second step (first desiliconizing operation) of a next step, and being therein nearly totally exhausted as concerns chromium oxide—it is conceivable that the amount of basic substances and especially of lime, which is to be used will be smaller for the obtention of a given final content of silicon, than in the previously known processes.

Practically, iron is present in the process by the mere fact that the ore of the alloying element contains iron. In the case of the manufacture of ferro-alloys, notably ferro-chromium iron is by nature present in the chromium ore (ilmenite). But iron can in any case be added to the process either in the furnace in which the primary alloy is manufactured or in the furnace in which the primary slag is fused.

On another hand, the primary slag made of oxidic compound or ore of the alloying element and of an oxide of a non volatile basic element may be obtained by fusing ore of the alloying element in the slag furnace and by adding thereto the basic oxide in the intermixing device.

It clearly appears from what is disclosed hereabove that owing to the combination of the two desiliconizing operations (second and third steps of the process) according to the invention, the amount of chromium ore to be used for the desiliconizing does not theoretically supersede the one which stoichiometrically corresponds, as concerns the reducible metallic oxides, to the amount of silicon which is to be eliminated, and that the said ore is totally exhausted as concerns chromium, during the second step of the process (first desiliconizing operation). No residual slag more or less rich in oxides, has thus to be treated

anew in the silico-chromium furnace, which allows as it has been disclosed above, to advantageously realize a running of the said furnace having an acid character.

It is to be remarked that if the three steps of the process according to the invention necessarily follow each other according to the sequence which has been indicated when they are considered as applied to the manufacture and the treatment of one and the same melt of silico-chromium, the carrying on of the process can however give rise to modifications as concerns the timely material succession of these three steps, as it is shown in the various embodiments hereabove described, these embodiments being disclosed as examples of practicing the invention.

First embodiment.—An appliance is used which comprises an electric furnace for the manufacture of silico-chromium alloy, a furnace for the fusion of chromium-ore and an intermixing apparatus made of two receptacles, each of them being open at one end, these two ends being closely united together in such a manner that the longitudinal axes of the two chambers make an angle of about 90° , and that there is a common lip for the two chambers over which the content of one chamber can be poured into the other chamber. These two chambers are mounted on a common oscillating axis—practically parallel to the said common lip—and means are provided for rocking the ensemble of the said apparatus and by these means energetically pouring the contents of one receptacle into the other and vice-versa.

The accompanying drawing diagrammatically shows such an appliance in which 1 is the tilting furnace for manufacturing the primary silico-chromium, 2 the tilting electric furnace for fusing the primary slag, 3 the rocking intermixing apparatus open at 4 and comprising two adjacent receptacles 5 and 6 having a common lip 56, pivoted on a horizontal shaft 7 carried by a double frame 8 and rocked by a motion device 9. Between the two parts 8 of the said frame is a pit 10 into which ladles 11 and 12 can respectively be sunk in order to cast the final ferro-chromium alloy poor in silicon and to discard the final slag poor in oxides. The primary silico-chromium and the primary slag are run into the intermixing apparatus respectively by means of the removable gutters 13 and 14.

The third step (second desiliconizing operation) of a preceding intermixing operation in the rocking apparatus 3 being supposed as terminated, the molten slag (intermediate slag) resulting of this step and which still contains substantial proportions of oxides (chromium and iron oxides) is left in the apparatus and a batch of silico-chromium alloy (primary alloy) manufactured in the silico-chromium furnace 1, is charged into the receptacle of the apparatus 3 in which the intermediate slag has been left. The silico-chromium can be introduced in the apparatus either in molten state or in solid state. The latter occurrence permits of rendering the functioning of the intermixing apparatus 3 timely independent of that of the silico-chromium furnace. After the intermixing of the silico-chromium and slag has been performed in the rocking apparatus and the silico-chromium has been partially desiliconized, the slag is allowed to separate from the metal and it is discarded, being practically exhausted as concerns oxides. It is then replaced in the rocking apparatus by molten chromium ore taken from the slag fusion

furnace 2 and a new operation of intermixing is carried on by progressively adding lime in solid state in the apparatus 3, thus forming primary slag. When the reaction between the partially desiliconized silico-chromium (intermediate alloy) and the mixture of chromium ore and lime (primary slag) is ended, the ferro-chromium which has been desiliconized to its final content of silicon, is cast and there remains in the intermixing apparatus 3 a molten slag (intermediate slag) which is ready for performing a second step of the process, i. e. a first desiliconizing operation of silico-chromium rich in silicon. In the said embodiment of the invention, the material sequence of the three steps of the process coincides with the one which characterises the scheme of the invention which has been described hereabove to set forth the invention.

Second embodiment.—An appliance is used which is the same as the one defined in relation with the first embodiment. In contradistinction with what has been the case in the first embodiment, the silico-chromium (intermediate alloy) which has been partially desiliconized by the second step of the process (first desiliconizing operation) is cast, allowed to solidify, crushed and stored in a storing place (not shown) after each operation. Partially desiliconized silico-chromium in crushed state is thus at hand in a permanent manner.

The sequence of the operations is in such a case, the following: a quantity of molten slag (primary slag having as a basis chromium-ore and lime) is taken from the slag fusion furnace 2 and is introduced into the intermixing apparatus 3 at the same time as partially desiliconized silico-chromium in crushed state taken from the storing place (intermediate alloy). An energetic intermixing is performed between the slag and silico-chromium and this intermixing desiliconizes the silico chromium to its final content of silicon, thus carrying on the third step of the process (second desiliconizing operation). The ferro-chromium thus obtained is cast after separating from the partially exhausted slag, the latter being kept in the apparatus 3 (intermediate slag). The necessary quantity of silico-chromium (primary alloy) is then taken from the silico-chromium furnace 1 and is introduced into the apparatus 3. The mixture of silico-chromium and slag is energetically intermixed therein in order to realize the total exhaustion of the slag as concerns Cr_2O_3 (second step of the process). Intermixing having been terminated, the slag is discarded in exhausted condition and the partially desiliconized silico-chromium (intermediate alloy) is cast; it is allowed to solidify and it is crushed and stored in view of being further treated later on.

It is to be remarked that in that second embodiment of the invention the sequence of the two desiliconizing steps in the intermixing apparatus is reversed in respect to the sequence which is followed in the first embodiment.

Third embodiment.—The appliance which is used is the same as the one hereabove described in relation with the first and second embodiments. As in the second embodiment the silico-chromium which has been partially desiliconized (intermediate alloy) during the performance of a second step of the process (first desiliconizing operation) is separated from the exhausted slag and it is cast, allowed to solidify and stored. The sequence of the operations is the following: Partially desiliconized silico-chromium (intermediate

alloy) is taken from the storage place and it is introduced in the slag fusion furnace 2 at the same time as the substances which compose the slag, principally chromium ore and lime. When these various substances are melted (primary slag and intermediate alloy) they are caused to react upon each other during such a long period of time that the final content of silicon which is wanted for the ferro-chromium alloy is reached (third step of the process)—second desiliconizing operation—the amount of chromium ore introduced in the slag fusion furnace 2 being so chosen that a relatively large quantity of Cr_2O_3 is left in the slag when the operation is ended. The ferro chromium obtained is separated from the slag and cast. The remaining slag (intermediate slag) is taken out of the fusion furnace 2 and it is introduced in the intermixing apparatus 3 at the same time as silico-chromium originated from the silico-chromium furnace 1 (primary alloy) and which can be charged either in liquid or in solid states. The mixture of silico-chromium and of the slag resulting from the previous operation is energetically intermixed during about two minutes, which realizes the second step of the process (partial desiliconization of the silico chromium and exhaustion of the slag as concerns Cr_2O_3 (first desiliconizing step). The exhausted slag is discarded and the partially desiliconized silico-chromium (intermediate alloy) is cast, allowed to solidify, crushed and stored in view of being further desiliconized.

In such an embodiment, as in the precedent one, the order of sequence of the two desiliconizing operations is timely reversed with respect to the one in which they follow each other in the first embodiment of the invention.

Below is given a detailed and still more specific example of carrying on the process according to the process of the invention.

A ferro-silico-chromium (primary alloy) having the following composition:

Si=45%
C=0,030%
Cr=40%

the remainder being substantially iron, was manufactured in a silico-chromium electric furnace, by starting of a charge comprising:

	Parts in weight
Chromium ore.....	about 150
Quartz	190
Coke	98

On the other hand, a mixture comprising 103 parts in weight of chromium ore and 80 parts in weight of lime, was melted in a slag fusion furnace and constituted a desiliconizing slag (primary slag).

In an intermixing apparatus such as the one hereabove described in relation with the first embodiment of the invention, 1500 kgs of the above said primary slag were charged together with 410 kgs of partially desiliconized ferro-silico-chromium intermediate-alloy resulting from a preceding operation according to the invention, and having the following composition:

Si=33%
Cr=51%
C=0,027%

the remainder being substantially iron. This ferro-silico-chromium had been allowed to solidify; it had been crushed beforehand so as to

wholly pass through a sieve the square meshes of which had opening dimensions of 5 mm.

After an energetic intermixing during two minutes, in the intermixing apparatus, about 560 kgs of ferro-chromium were obtained having the following composition:

Si=0,12%
C=0,024%
Cr=73,50%

the remainder being substantially iron.

The so obtained ferro-chromium which had very low content of silicon and carbon was cast as final product of the process, and the slag (intermediate slag) was left in the intermixing apparatus.

The said slag had the following composition:

Cr₂O₃=7%
SiO₂=25%
FeO=0,20%
Al₂O₃=9,50%
CaO=46%
MgO=11,50%

the remainder having not been determined by an

analysis as it was of no importance to know the composition thereof.

To this intermediate slag 365 kgs. of molten ferro-silico-chromium taken from the silico-chromium electric furnace above referred to and the composition of which has been given here-above (primary alloy), were added in the intermixing apparatus.

After two minutes of energetic intermixing in the rocking apparatus 395 kgs of partially desilicized ferro-silico-chromium (intermediate alloy) were obtained, the analysis of which was:

Si = 33%
Cr = 52%
C = 0,027%

This intermediate ferro-chromium was separated from the slag, allowed to solidify, crushed and stored.

The slag was then discarded; it contained but 0,5% of Cr₂O₃ and 0,14% of FeO, being accordingly perfectly exhausted as concerns reducible oxides.

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