PROCESS IN SELECTIVE REDUCTION OF CHROME ORE

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3 Claims. (Cl. 75—11)

The present invention relates to a process in selective reduction of chrome ore containing chromium and iron compounds and having a low ratio of chromium to iron by means of a reducing agent containing silicon and in some instances iron to produce a slag phase having a substantially greater ratio of chromium to iron.

In producing chromium alloys substantially intended for manufacture of steel, chrome ores with a ratio between the amount of chromium and iron of 3:1 are normally used. Thereby the ores are obtained which have an amount of chromium of 65—75%. Particularly in the production of stainless steel (the amount of chromium being greater than 13%) it is helpful to use a ferro-alloy containing a great amount of chromium, as the amount of the ferro alloy thereby can be kept comparatively low, which is important from the viewpoint of production. For these reasons it has become practice to use chrome ores with a ratio of about 3:1 for metallurgical purposes. However, ores of this kind are scarce, and therefore attempts have been made to find ways of using ores with a lower ratio for the production of ferro alloys. There are, for example, large supplies in the world of chrome ores with a ratio of about 1:6—1. However, according to conventional methods, chromium alloys with ordinary amounts of chromium cannot be made from these ores. Several inventors have been occupied with the problem of producing a slag melt with increased ratio of iron to chrome with a low ratio through selective reduction of iron, which melt thereafter is reduced in accordance with well known methods. This selective reduction is possible because iron has a lower affinity to oxygen than chromium and thus can be removed to a considerable degree before the reduction of chromium has gone too far.

As a reduction agent at the selective reducing (or pre-reduction) as it may be called) carbon and silicon have above all been proposed. The latter reducing agent has been proposed as preferably used in the form of a silicon-iron alloy for economical reasons, as it is expensive to produce pure silicon. Also other reducing agents with great affinity to oxygen can be used, such as for example Al and Mg. They are too expensive, however. Carbon is a cheap reducing agent, but the disadvantage is that after the pre-reduction there may be residues of the reducing agent in the slag melt, which at the final reduction can easily cause an increase of the amount of carbon in the alloy. Therefore carbon must be considered an unsuitable reducing agent in this connection, at any rate when an alloy with a low amount of carbon is desired. Thus, silicon seems to be the most suitable material for selective reduction, and therefore only pre-reduction with silicon will be hereinafter described.

The following conditions should be present with regard to a process for pre-reduction for the purpose of increasing the ratio of the ore:

(a) The reduction of iron from the ore melt shall be driven to the desired ratio with as small simultaneous reduction of chromium as possible.

(b) As small an amount of silica as possible shall be added to the ore melt during pre-reduction, as the subsequent final reduction requires a high basicity in the slag melt if it shall be carried through technically-economically in the right manner.

(c) The reducing agent shall be cheap and easily available.

The metal phase obtained by pre-reduction is substantially a ferrous alloy, the amount of chromium being about 15—25%. The amount of chromium in the metal phase depends upon how far, that is to say that ratio in the slag melt the pre-reduction has been driven.

In case the pre-reduction is carried out with a silicon-iron containing about 50% of silicon, the result will be that the condition stated under (a) cannot be fulfilled, as a considerable amount of chromium is reduced. Per unit of weight of iron reduced 0.2—0.3 units by weight of chromium are reduced, and, in addition, 0.2—0.3 units by weight of chromium are reduced per unit of weight of iron added in the silicon iron. Neither is the condition stated under (b) fulfilled owing to the strong reduction of chromium, as silica is then added to the slag phase. The condition stated under (c) is fulfilled, but this is far from counterbalanced by the disadvantages according to (a) and (b).

If silicon metal is used at the pre-reduction it will be seen that the reduction of chromium is smaller than in the preceding case, as no iron is added. The condition stated under (a) is thus better fulfilled. Due to the fact that in this case a smaller amount of chromium is reduced, the silicon metal fulfills the condition under (b) better than the 50—percent silicon iron. On the other hand, the condition stated under (c) is not fulfilled, as silicon metal is expensive.

In the present invention silicon can be used in the form of a silicon alloy as a reducing agent, but in spite of all the above conditions can be fulfilled. Thus, the present process refers to a special way of carrying out the pre-reduction, silicon being used as reducing agent.

The process is substantially characterized in that the reducing agent also contains chromium. The amount of chromium ought to be between 10 and 60% by weight, preferably between 20 and 45% by weight and suitably between 25 and 40% by weight.

There should be so much chromium in the reducing agent that substantially only iron and other easily reducible compounds can be reduced from the ore, chromium thus remaining. Chromium should preferentially not be added in such an amount that it serves as the chief reducing agent, which shall be silicon.

The process can be carried out in the following manner: The ore is charged in a furnace, preferably an electric arc furnace, together with burned lime or some other basic fluxing agent. The mixture of ore and lime can be supplied in the form of a melt. The reducing agent is supplied in solid state or as a melt and it may be supplied at any stage of the process. It may be supplied together with the mixture of ore and lime, when charging, or after the latter is melted. Usually the reducing agent ought to contain between 40 and 75% by weight, of Si, but the amount may be lower. It need not contain iron, but available chromium-silicon alloys normally contain Fe in amounts between 5 and 30% by weight. The ratio between the amounts of Cr and Fe of the reducing agent ought to be at least that which is obtained if the reducing agent is produced in one or two steps, from the ore concerned, that is, usually higher than 1.0:1, preferably above 1.2:1. When the reaction has gone so far that the ratio intended is attained in the slag melt, either the slag phase or the metal phase or both phases are tapped. It may occur that the slag phase contains a considerable quantity of metal in the form
of suspended small drops. As the ratio of the metal phase is very low the possibility of obtaining a satisfactory ratio in the slag is jeopardized. In such a case it may be necessary, after finely dividing the solidified slag, to rid the latter of its metal inclusions by magnetic separation or in some other well-known manner.

The amount of reducing agent depends substantially on the ratio of the ore used and the desired ratio in the slag and on the composition of the reduction agent.

The ores which according to the invention are to be refined have a ratio which usually is between 1.3 and 2.0. However, if not outside the scope of the invention to treat ores of both higher and lower ratio. The desired ratio of the slag to be produced is preferably between 2.8 and 3.5, but of course slags can be produced both of higher and lower ratio.

If the difference between the ratio of the ore used and the desired ratio of the slag is great, and if the amount of silicon and the amount of chromium in the reducing agent are low, a great amount of reducing agent is required, for example 200 kg. per 1000 kg. of ore, and the other way around, if the difference is small and the amounts of Si and Cr are high, an amount of 50 kg. of reducing agent per 1000 kg. of ore may be sufficient. Under ordinary circumstances an amount of 60-140 kg. per 1000 kg. of ore should be sufficient.

Several advantages are gained by the process according to the invention. At the pre-reduction the reduction of chromium from the ore melt is kept back through the increase of the activity of the chromium in the metal phase which is a result of the fact that chromium is included in the reducing agent. It is possible to adjust the amount of chromium in the reducing agent so that the whole amount of chromium in the ore is maintained in the ore melt during the pre-reduction. If the amount of chromium in the reducing agent is increased beyond this value, chromium will, to a certain extent, serve as a reducing agent for the iron oxide in the ore melt. If, on the other hand, the amount of chromium in the reducing agent is reduced below the said value, a certain reduction of chrome oxide in the ore melt will take place. Thus, as it is possible, according to the process, entirely to avoid reduction of chromium at the pre-reduction the condition stated under (a) is fulfilled. In such a case only a reduction of iron from the ore melt is obtained at the pre-reduction. The amount of silica added to the ore melt is equivalent with the amount of iron reduced and can thus not become smaller when silicon is used as reducing agent. Thus, also the conditions stated under (b) are fulfilled. It must be pointed out that when the amount of chromium in the reducing agent is higher than that value at which the reduction of chromium from the ore melt is entirely suppressed, the amount of silica of the ore melt will increase still less during the pre-reduction, as in such a case some of the reduced iron is obtained through reduction of iron oxide with metallic chromium. Thus, in this case a conversion of chromium from the metal phase to the ore melt takes place.

In a process according to the invention it is further possible to use, at the pre-reduction, the same reducing agent containing silicon and chromium, which normally is used in the production of super-refined (suraffiné) chromium according to well-known processes. This alloy has normally an amount of silicon of about 50%, and therefore it is cheap to manufacture. Furthermore the advantage is gained that the same reduction agent can be used both at the pre-reduction and at the final reduction. Thus, also the conditions stated under (c) are fulfilled.

In the following an example is given of a process according to the invention, beside which an example of the use of a chromeless silicon-iron alloy containing approximately the same amount of silicon is given for the sake of comparison.

### The composition of the chrome ore:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cr₂O₃</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent</td>
<td>44</td>
<td>18.9</td>
<td>9</td>
<td>3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

300 kg. of ore (dry weight: 290 kg.) were melted in an electric arc furnace of 300 kw. together with 200 kg. of burnt lime of the following composition:

- CaO, 86%; MgO, 2%; SiO₂, 3%; ignition loss, 5%

An ore-lime melt of the following composition was obtained:

| Cr₂O₃ | 27.2
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>11.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>37.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5.6</td>
</tr>
</tbody>
</table>

To this melt 30 kg. of reducing agent were afterwards added in the form of a silicon-iron-chrome alloy of the following composition:

- Si, 49.3%; Cr, 28.4%; Fe, 21.3%

After a period of 40 minutes metal and slag were tapped. The amount of metal was 38 kg. and the amount of slag was 448 kg.

The metal had the following composition:

- Cr, 15.3%; Si, 0.07%; Fe, 83%; C, 0.1%

The slag had the following composition:

- Cr₂O₃, 29.5%; FeO, 8.5%; SiO₂, 12.9%; ratio, 3.1:1

### Balance of chromium and iron:

<table>
<thead>
<tr>
<th>Kg. Cr</th>
<th>Kg. Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>Metal</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>Added;</td>
<td></td>
</tr>
<tr>
<td>Ores</td>
<td></td>
</tr>
<tr>
<td>silicon-chromium</td>
<td>87.6</td>
</tr>
<tr>
<td>Total</td>
<td>96.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kg. Cr</th>
<th>Kg. Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removed;</td>
<td></td>
</tr>
<tr>
<td>Metal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.9</td>
</tr>
<tr>
<td>Total</td>
<td>96.1</td>
</tr>
</tbody>
</table>

Of the total amount of Cr added 5.8% entered the metal phase. As will be seen 31.5-6.4, that is, 25.1 kg. of Fe was reduced, first of all by Si supplied but also by Cr supplied. In addition to reduction of Fe a reducing agent was used for the reduction for example of P and Ni and for the reduction of certain metal oxides from higher to lower stages of oxidation, for example from Fe₂O₃ to FeO. If we presume that Cr only participated in the reduction of FeO to Fe and that Si participated in all the reductions, then the following result would be obtained:

- 8.5 - 5.8 = 2.7 kg. of Cr reduced
- 2.7 kg. of Fe reduced
- 2.5 kg. of Fe reduced
- 2.0 kg. of Fe reduced
- 20.75 kg. of Si reduced

The remaining of reduced Fe 25.1 - 4.35 = 20.75 kg. required for reduction from FeO to Si

<table>
<thead>
<tr>
<th>Fe</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.75</td>
<td>28.06</td>
</tr>
<tr>
<td>20.75</td>
<td>5.20 kg. of Si</td>
</tr>
</tbody>
</table>
Thus, of totally supplied Si=30.0.493=14.8 kg. (14.8
-5.2=9.6 kg.) were consumed for other reductions than
FeO to Fe and losses as reaction with oxygen.

Starting from the above example we will calculate
what result would have been obtained if silicon-iron con-
taining 50% of silicon had been used.

Composition of silicon-iron: Si, 50%; Fe, 48%.

It is presumed that an amount of x kg. ferrosilicon is
required for bringing about a ratio of 3:1:1 in the ore
melt, an amount of y kg. of metal phases being then ob-
tained.

\[
\begin{align*}
87.6 - y & = 0.153 \\
54.6 + & x = 0.48 - y = 0.83 \\
(x - y) & = 41.4 \\
y & = 59.5
\end{align*}
\]

Then an amount of silicon-iron of 41.4 kg. is required,
and the amount of metal obtained will be 59.5 kg. The
weight of the slag melt after the pre-reduction then will be:

\[
448 + (38 - 30) = (59.5 - 41.4) = 437.9 \text{ kg.}
\]

Balance of chromium and iron.

<table>
<thead>
<tr>
<th>Kg. Cr</th>
<th>Kg. Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>Metal</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>Supplied:</td>
<td></td>
</tr>
<tr>
<td>Ferrosilicon</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>Removed:</td>
<td></td>
</tr>
<tr>
<td>Ore melt</td>
<td></td>
</tr>
<tr>
<td>Metal</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>

The composition of the ore melt will be:

\[
\begin{align*}
\text{Cr}_2\text{O}_3, & \quad 26.2\%; \quad \text{FeO}, \quad 7.4\% \\
\text{SiO}_2, & \quad 16.1\%; \quad \text{ratio}, \quad 3:1:1
\end{align*}
\]

The ore-lime melt obtained after the pre-reduction is
hardly fitted for manufacture of ferro-chromium affinity.

The amount of \(\text{Cr}_2\text{O}_3\) is low, 26.2%, whereas the amount
is 29.5 according to the invention. Still worse, however,
is the great amount of \(\text{SiO}_2\), 16.1% to 12.9%, or 61.5%
to 43.7% of the amount of \(\text{Cr}_2\text{O}_3\) of the melt.

What we claim is:

1. A process for upgrading the chrome content of a
chrome ore having a ratio of chromium to iron of less
than about 2 to 1, comprising melting said chrome ore
in an electric arc furnace, to form a molten bath of said
ore, adding a basic fluxing material to said molten bath,
introducing into said bath a reducing agent consisting
essentially of between about 20% and 45% chromium,
between about 40% and 75% silicon and up to about
50% iron, said reducing agent acting selectively to re-
duce to metallic iron a substantial portion of the iron
oxide in said ore to form a metal phase containing prin-
cipally iron and to suppress the reduction of chromium
oxide and form a slag phase containing substantially all
of the chromium oxide initially present in said ore and
a substantially smaller quantity of the iron oxide initially
present in the ore, and separating said slag phase from
said metal phase.

2. A process for upgrading the chrome content of
chrome ores as set forth in claim 1 in which the slag
phase has a chrome to iron ratio between about 2.8 to 1
and 3.5 to 1.

3. A process for upgrading the chrome content of
chrome ores having a chromium to iron ratio lower than
about 2 to 1, comprising melting said chrome ore and a
basic fluxing material in an electric arc furnace and add-
ing to the melt a reducing agent consisting essentially
of between about 40% and 75% silicon, between about
10% and 60% chromium and up to about 30% iron,
thereby to reduce a substantial part of the iron content
of the ore to metallic iron and to suppress reduction of
said chromium oxide to form a metallic phase containing
principally iron and a minor proportion of chromium
and a slag phase containing substantially all of the
chromium oxide initially present in said ore and a sub-
stantially smaller quantity of the iron oxide initially
present in said ore.

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<thead>
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<th>Date</th>
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