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PROCESS FOR THE PREPARATION OF FERROALLOYS

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The present invention relates to a process for the preparation of low-carbon ferroalloys, especially of ferrochromium with a carbon content not exceeding 0.08%, preferably ranging between 0.02% and 0.04%, and of ferromanganese with a carbon content of about 0.2%. In the preparation of ferrochromium and iron-silico-alloy with a medium silicon content and a carbon content of about 0.1% and in the preparation of ferromanganese an iron-silico-alloy with more than 0.1% of carbon are treated with oxygen or oxygen-containing gases and are refined by means of a mixture consisting of chromium ore and lime or of manganese ore and lime. The slag is then separated and the ferroalloy is further treated with oxygen or oxygen-containing gases.

The processes employed at present for the production of low-carbon ferroalloys, especially of ferrochromium and ferromanganese, are customarily carried out either in one step or in two steps and lead to a silicon-containing alloy of a varying silicon content ranging from 15 to 60% through a carbon-containing prealloy. The carbon content remaining in the alloy depends on the amount of the silicon content. This alloy known as silicoalloy is then reacted with mixtures consisting of chromium ore or manganese ore and slag formers to yield a ferroalloy. In this process the silicon is used for reduction of the heavy metal oxides.

Other processes are carried out in a solid phase and the carbon is removed by oxidation under a very reduced pressure.

There are also known processes for the elimination of impurities from silicon alloys, wherein the proportions of aluminum, carbon, hydrogen, nitrogen, and phosphorus in the alloys are reduced by blowing oxygen or oxygen-containing gases on to the surface of the melt or by passing or blowing them through the melt, without the silicon being essentially oxidized.

According to another process the major part of the silicon is slagged off from low-carbon silicon alloys by means of lime and ores or metal oxides. The further elimination of silicon is then effected by oxidation with gaseous oxygen.

Now we have found that a combination of the two last-named processes results in a considerable improvement of the hitherto used methods for the preparation of ferroalloys with a low carbon content.

Thus it is possible to prepare especially low-carbon ferroalloys, in particular ferrochromium with a carbon content not exceeding 0.08%, preferably between 0.02 and 0.04%, and ferromanganese with a carbon content of about 0.2% in the following way: An iron-silico-alloy with a medium silicon content and a carbon content not exceeding 0.1% in the case of ferrochromium and with a carbon content of above 0.1% in the case of ferromanganese is treated with oxygen or oxygen-containing gases, is thus reduced to the desired low contents and refined by means of a mixture consisting of chromium ore and lime or manganese ore and lime. After the desiliconization is thus attained, the slag is separated and the ferroalloy is further treated with oxygen or oxygen-containing gases in order to obtain lower proportions of silicon, nitrogen, and other impurities.

In an especially advantageous modification of the process for the preparation of ferromanganese, and iron-manganese-silicon-alloy with a medium silicon content of preferably 20–30% is used. The ratio of manganese to iron in this alloy is 2.2:1 and the carbon content ranges between 0.5–1.5% in correspondence with the silicon content.

When using raw materials which are poor in aluminum, the aluminum content of the silicoalloy can be increased to at least 1% by addition of alumina-containing materials. Alumina-containing quartzite is particularly suitable for this purpose.

Finally, it is also possible to use, instead of aluminum, titanium or zirconium in the form of titanium- or zirconium-containing additions and thus to raise the content of titanium or zirconium in the silicoalloy to at least 1%.

The process of the present invention will be illustrated by means of the following examples:

1. *Preparation of ferrochromium*

A silicochromium which contains between 35 and 45% of silicon is prepared in the usual manner, whilst the processes hitherto known require 50–55% of silicon.

This alloy containing 35–45% of silicon is treated, in a vessel with an acid lining, for instance a converter, an electroconverter or in a similar device, with oxygen or oxygen-containing gases, whereby the original carbon content of about 0.05–0.1% is reduced to 0.008% at least, however, to 0.04%. At the same time 1–2% of the silicon content are burnt and form a silicon slag.

This process is best carried out at temperatures above 1600° C. The silicochromium so treated is desiliconized in known manner in the same vessel or after transferring it into another vessel with a mixture consisting of chromium ore and lime. The desiliconization process is retarded in accordance with the falling silicon content. For this reason, the refining process is broken off when a residual content of about 5–10% of silicon is left. The slag obtained which contains about 5% of chromium oxide is drawn off or poured out. It is discarded since it contains only little chromium oxide.

After having drawn off the slag, the ferrochromium which still contains 3–5% of silicon is treated with gaseous oxygen while adding such a quantity of lime that a lime silica slag forms having a basicity of at least 1.2–2.0. The content of chromium oxide of this slag is very low. Thus, the slag can likewise be discarded.

The advantage of the new method of working resides in the fact that by the treatment with gaseous oxygen the speed of oxidation of the silicon is considerably increased. A further advantage resides in the fact that the nitrogen content of the ferrochromium alloy is reduced at the same time.

If, in the preparation of the silicochromium, alumina-containing quartzite is used, the aluminum content of the alloy can be raised to 1–2% or more. Thus, it is achieved that, instead of silicon, aluminum is oxidized in the first step of the treatment. In addition, the decarbonization to the desired lowest content is accelerated by the initial content of aluminum, since the oxidation of aluminum produces a desired increase in the temperature.

The same effect can be attained if titanium or zirconium are contained in the silicoalloy in similar quantities.

2. *Preparation of ferromanganese*

The same conditions apply as in Example 1. However, the reduced carbon content in the finished alloy need only amount to 0.5% max. and, in exceptional cases, to 0.1%. Therefore, the initial contents of silicon in the silicoalloy

need not be so high since the carbon content in ferroalloys depends on the silicon content of the alloy.

A silicoalloy with 20–22% of silicon and a ratio of manganese to iron of about 2.2:1 is prepared in known manner. The same operations are carried out as described in Example 1. The oxidizing refining process of the silicoalloy leads to a reduction of the carbon content from about 1% to 0.5% max. When the silicon content has been reduced to about 3–5%, the refining process is broken off and the residual silicon is eliminated by means of oxygen.

If the ferromanganese is to contain 0.1% of carbon, the silicon content of the initial alloy, that is to say of the silicoalloy, must be raised to 25–30% if the same ratio of manganese to iron applies.

In order to meet the present-day requirements it is obvious that the desiliconization of the silicomanganese must be carried out with a high-grade manganese ore. The residual silicon is removed by means of oxygen as described above.

The advantage of the process according to the present invention resides in the fact that the desired carbon content is definitely attained. In addition, the process claimed by us is more economical owing to the lower consumption of electric energy since 5–10% less of silicon need be removed.

We claim:

1. The process of preparing a ferroalloy selected from the group consisting of ferrochromium containing a maximum carbon content of 0.08% and ferromanganese containing a maximum carbon content of approximately 0.2% comprising the steps of treating, at a temperature above 1600° C., a member of the group consisting of an iron-silico-alloy of medium silicon content containing at least 1% by weight of a reducing metal, and a mixture of an iron-silico-alloy of medium silicon content and at least 1% by weight of a reducing metal, said reducing metal being selected from the group consisting of aluminum, titanium and zirconium, with oxygen to obtain the desired carbon content, refining the resulting alloy with a mixture consisting of lime and an ore of the selected alloying metal, separating resulting slag and treating resulting ferroalloy with oxygen to lower the silicon, nitrogen and other impurity content.

2. The process of preparing a ferrochromium alloy containing a maximum carbon content of 0.08% comprising the steps of treating, at a temperature above 1600° C., a member of a group consisting of an iron-silico-alloy of medium silicon content containing at least 1% by weight of a reducing metal, and a mixture of an iron-silico-alloy and at least 1% by weight of a reducing metal, said reducing metal being selected from the group consisting of aluminum, titanium and zirconium, said member having a carbon content of less than 0.1% with oxygen to obtain the desired carbon content, refining the resulting alloy with a mixture consisting of lime and chromium ore, separating resulting slag and treating resulting ferroalloy with oxygen to lower the silicon, nitrogen and other impurity content.

3. The process of preparing a ferromanganese alloy containing a maximum carbon content of 0.2% comprising the steps of treating, at a temperature above 1600° C., a member of a group consisting of an iron-silico-alloy of medium silicon content containing at least 1% by weight of a reducing metal, and a mixture of an iron-silico-alloy and at least 1% by weight of a reducing metal, said reducing metal being selected from the group consisting of aluminum, titanium and zirconium, said member having a carbon content of more than 0.1% with oxygen to obtain the desired carbon content, refining the resulting alloy with a mixture consisting of lime and manganese ore, separating resulting slag and treating resulting ferroalloy with oxygen to lower the silicon, nitrogen and other impurity content.

4. The process of preparing a ferromanganese alloy containing a maximum carbon content of approximately 0.2% comprising the steps of treating, at a temperature above 1600° C., a member of the group consisting of an iron-manganese-silicon-alloy of a medium silicon content containing at least 1% by weight of a reducing metal, and a mixture of an iron-manganese-silicon-alloy of medium silicon content and at least 1% by weight of a reducing metal, said reducing metal being selected from the group consisting of aluminum, titanium and zirconium, having a carbon content of from 0.5% to 1.5% and a maximum ratio of manganese to iron of from 2.2 to 1 with oxygen to obtain the desired carbon content, refining the resulting alloy with a mixture consisting of lime and manganese ore, separating resulting slag and treating resulting ferroalloy with oxygen to lower the silicon, nitrogen and other purity content.

5. The process of claim 4 wherein the silicon content of the iron-manganese-silicon-alloy is from 20 to 30%.

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