METHOD OF PRODUCING IRON OR STEEL ALLOYS

The present invention, which is a continuation in part of our copending application Serial No. 756,823, filed June 24, 1926, relates to a method for producing alloys of metals belonging to the iron group, and especially alloys of iron, directly out of oxide ores of said metal and oxide ores of the alloy constituents, with the use of carbon as a reducing agent. The carbon, if desired, may be partly replaced by other reducing agents such as ferro-silicon, ferro-manganese or aluminium.

The expression "alloys of iron" comprises all alloys containing iron, ranging from, on the one hand, alloys in which iron is the main constituent, that is to say, iron or steel which in addition to the iron contains one or more other metals which impart special desirable properties to the iron, such properties being such as are not possessed by carbon-iron or carbon-steel alone; to, on the other hand, alloys in which iron is present to a relatively less extent as in, for example, ferro-manganese, ferro-chromium, ferro-manganese-silicon, or the like.

In iron works it often happens that in one heat or smelting an alloyed iron or steel containing a certain percentage of, for instance, chromium, is to be produced and that in a following heat an alloyed iron or steel containing a different percentage of chromium will have to be manufactured. In such cases it has been necessary, prior to our invention disclosed in said copending application and prior to the present invention, to make up a special charge for every different percentage of chromium in the alloyed metal, which, of course, requires several corresponding charges of different compositions. It has also been proved to be rather difficult to regulate the percentage of alloy constituent within narrow limits by simply varying the composition of the charge.

The method disclosed in our copending application, Serial No. 756,823, of which this is a continuation, obviated the above inconvenience to such extent that it represented a distinct advance in the art. The method consisted chiefly in making up separate mixtures of finely ground portions of each one of the ores with carbonaceous material of a quantity proportioned to the reduction of the ore and to the desired percentage of carbon in the final product, and melting these mixtures in a furnace, with the quantities of the mixtures so proportioned to each other as to obtain an alloy of the desired composition.

Now it is well known that chromium ore, when reduced by carbonaceous reducing agents, always produces a product which is more or less contaminated with carbon, so that further refinement is necessary. For this reason, inventors and experts in the metallurgical art have, prior to our inventions, found it necessary first to produce a high carbon product, and thereafter to remove the excess carbon by the addition of ore or by other means. These two-stage processes are necessarily costly and result in a considerable loss of alloying metal.

It is the principal object of the present invention to perfect the process disclosed in our application, Serial No. 756,823 and briefly described above so that the foregoing disadvantages will be entirely obviated. This we have done and we are able at will to produce predetermined low carbon alloys directly while using a carbonaceous reducing agent. Our improved process will now be described in detail.

The invention comprises forming separate mixtures of the oxide ore of the base metal, for instance, iron, and of the oxide ore of the alloy constituent together with carbon-containing reducing agent of a quantity proportioned to the reduction of the ore and to the desired percentage of carbon in the metal therefrom and reducing and melting said mixtures whilst floating on top of or in a slag bath in an electric furnace whilst pro-
portioning the quantities of the mixtures to each other so as to obtain an alloy of the desired percentage of the alloy constituent.

The expression "carbon-containing reducing agent" is understood to comprise, on the one hand, all sorts of carbon, for instance, char-coal, pit-coal, anthracite, coke or the like; on the other hand, however, also any mixture of carbon with another reducing agent or agents, such as ferro-silicon, ferro-manganese, ferro-aluminum-silicon, aluminum or the like, provided such other reducing agent be added only in such proportion, that the carbon is the main constituent and that the process will remain endothermic.

While the mixtures may consist of finely ground and intimately mixed loose material, we prefer to transform each of them into a solidified state by mixing the corresponding oxide ore in a finely divided state with carbon-containing reducing agent in a finely divided state and transforming said mixture into briquettes or any other form of bodies in known manner. The smaller the size of the grains of the ore and particles of the reducing agent, such as carbon, that is to say, the closer the size of the grains approaches the molecular size the better the method is effected. In the briquettes the particles of the reducing agent and the grains of the ore should be distributed as uniformly as possible and the mass should be of such consistency as will prevent segregation of its constituents.

If required or found suitable for obtaining a more solid adhesion of the grains, adhesives of known kind may be used in the process of transforming the materials into solidified state but in such case, provided carbonaceous adhesives are used, the total quantity of carbon useful for the reduction in the various kinds of charge should be so adapted that the desired percentage of carbon is obtained in the final product. In some instances the charges or briquettes are dried prior to being introduced into the electric furnace, in air or some other atmosphere, for instance, an atmosphere containing carbonic acid, when using lime or lime-white as an adhesive and a reagent. Thus, if liquid carbonaceous reducing material or liquid adhesive has been added, the mass will be dried so that these materials become solid and keep the particles of the ore and those of the reducing agent together in fixed relation. By the drying process any contents of water that may be present are expelled, so that bursting of the briquettes or bodies through steam developed by the heat in the furnace cannot take place.

If, to facilitate a very intimate mixing of the particles of the ore with those of the reducing agent and any adhesive added, a certain percentage of water has to be added, it may be preferred only to partially dry the mixture prior to the briquetting process which is best carried out with a certain percentage of water in the mixture.

Obviously, if a plurality of metals are to be alloyed with the iron, separate charges, preferably in the form of solidified bodies, may be prepared from the ores of each of each of said metals or a charge may be prepared from a suitable mixture of these ores.

The charge of the base metal, for instance, iron ore, may be reduced and melted in admixture with the alloy charge, but in practical working, particularly when a plurality of iron alloys of different qualities and characteristics are to be produced, it may be preferable to modify this method of production somewhat. The charge of the base metal and that of the alloying metal being reduced and melted, not admixed with one another, but successively in an arbitrary order, and the metals are then alloyed with each other in the furnace. The quantity of each kind of charge is determined for the desired composition of the final product and it will then be found easy during working to take tests to ascertain whether the desired proportions have been obtained, and by an increased addition of the one or the other kind of charge to control the final composition of the product.

Of course, such a furnace practice may also be applied when reducing and melting an admixture of different kinds of charge. Thus, by controlling the quantity fed in of each kind of charge, alloys having different percentages of the alloying metal or metals may be readily produced without varying the composition of each kind of charge. If only a small quantity of other metal is to be alloyed with the base metal, it is preferred first to reduce the base metal out of the base metal charge in the manner set forth, and then to reduce the metal or metals to be alloyed with the base metal out of the alloy charge or charges. With greater percentages of alloying metal that order is used between the different kinds of charge which is found most advantageous in each individual case.

In ordinary cases deoxidizing of iron or steel is effected by the addition of deoxidizing metals, generally ferro-manganese or ferro-silicon or both, and such deoxidation may be applied also to our present process at any desired time during a smelting. It is preferred, however, to prepare briquettes or other bodies in the manner previously set forth, out of oxide ore of a metal adapted to be used as a deoxidizing agent, especially manganese, such briquettes being reduced and melted on the slag bath in the furnace when deoxidation of metal or slag or both is to be effected. The deoxidizing metal reduced in this process then removes from the alloy previously obtained in the furnace a greater or smaller part of its
oxygen, and is transferred into the slag formed in melting. The slag, however, is also deoxidized, so that, for instance, when using briquettes of manganese ore, oxides of metals present in the slag and having a smaller affinity to oxygen than manganese are reduced out of the slag, more or less completely, and are absorbed by the metal obtained at the bottom of the furnace. In producing, for instance, so called rustless iron and steel holding 9–10% Cr and below 0.7% C, the consumption of chromium charge for a given quantity of alloy will be considerably smaller if reduction is effected in the manner set forth. If not, such reduction will take place with the chromium first reduced out of the slag, which chromium is thus lost in the slag. As the chromium ore is much more expensive per unit of oxygen absorbed from the slag than is, for instance, manganese ore, a considerable saving will be attained in this manner.

The reduction and melting should preferably take place with the electrode or electrodes out of contact with the charge or charges, especially when using carbon electrodes, and by the aid, at least in part, of electric resistance heat developed in the slag, the charge or charges being reduced and melted whilst floating on or in said slag as is more fully described in our Patent No. 1,686,306. The present invention takes the process of that application several steps further, in that, instead of one charge, two or more charges are used, for example, an iron charge and a chromium charge, and these two charges are so proportioned to each other as to produce the desired alloy directly. Our success in producing these alloys, particularly the lower carbon alloys, such as stainless iron, directly, where prior inventors have failed, appears to be due in great part to the fact that in the present process the charge is reduced and melted while floating on the top of or in a slag bath in an electric furnace with the aid, at least in part, of electric resistance heat developed in the slag and that the particles of ore and carbon are mixed in correct proportions in intimate contact with one another, which contact is maintained during the course of the reaction.

In reducing and melting the different kinds of charge in succession, it is preferred in some cases, after one kind of charge has been reduced and melted wholly or partly to draw off the slag thus formed out of the furnace, before treatment of the next kind of charge is commenced. The reasons for this are different. In ores of comparatively expensive metals, a considerable saving may be attained in this manner, owing to slugging of the expensive metal to a less extent, in that a smaller quantity of slag than otherwise is saturated in the furnace with oxides of this metal. If some or more of the oxide ores hold sulphur to such an extent that the percentage of sulphur in the metal produced would be higher than desirable, it is preferred first to reduce and to melt the charge or charges containing this ore or these ores respectively, and then wholly or partly to draw off the slag obtained for removing the sulphur absorbed in the same. Prior to tapping the slag the same may be deoxidized in the manner hereinafore set forth, or in some other way, for instance, by the addition of lime and carbon and by working with the electric arc, so that carbide of calcium is formed, in order to reduce the percentage of metal of the slag, and to increase its capability of absorbing sulphur. By tapping the slag intervening with the melting of the different kinds of charge, the phosphorus transferred into the slag may also be removed from the furnace, before the same would, perhaps, be reduced and absorbed in the metal in the treatment of the other kind of charge.

By controlling the total percentage of carbon in the different kinds of charge, a product having the desired percentage of carbon may be produced directly. The desired percentage of carbon in the product may also, however, be obtained by controlling the percentage of carbon in the kind of charge out of which a metal having a low percentage of carbon may be most readily produced, thus, for example, in the iron ore charge, so that a metal having a low percentage of carbon is first obtained, that is to say iron, in the example given, and then adding the other kind or kinds of charge having a percentage of carbon so adapted that the final product will have the desired percentage of carbon. If, however, products having different percentages of carbon are to be produced, it is more simple to use charges in which the total quantity of carbon has been adapted so that a product of alloyed iron or steel or an alloy as low in carbon as possible is obtained which is then carburized to the desired percentage of carbon in the furnace or outside the same. Preferably this carburization may also be effected by introducing into the furnace and by reducing and melting, in a final process, a certain quantity of any of the kinds of charge having an adapted higher percentage of carbon.

If in addition to being alloyed with one or more alloy materials, the iron is also to be alloyed with some or other metal in a smaller or a negligible quantity, such metal may preferably be added in known manner in a metallic state to the alloyed iron reduced in the furnace, either in the furnace or outside the same, for instance in a ladle or another furnace. In the same manner, an iron alloy or the like having approximately the proper percentage of the desired alloy substances, such iron alloy being produced directly out of oxide ores according to the invention, may preferably be admixed with such alloy...
substances in a metallic state in known manner in or outside the furnace, for the purpose of providing a final control of the percentages of these substances in the final product.

The method according to the invention is particularly adapted for production of so-called alloyed iron or steel having relatively high percentages of alloy substances, such as manganese steel, chromium steel, tungsten steel, etc. which in this manner may be produced at a much lower cost than in the methods hitherto practised for the production of such alloyed irons and steels. In order not to attain too high percentages of carbon in the final product, the alloy substances, as a matter of fact, hitherto had to be added to the iron in the form of very expensive low-carbon alloys of these substances. With the application of this method, for example, so-called rustless iron or steel, that is to say, an iron having a rather high percentage of chromium or about 9–16%, and a rather low percentage of carbon, or below 0.7%, may be produced directly. No difficulty will be experienced with this method in directly producing an iron holding, for instance, about 14% Cr and below 0.1% C which, without further treatment, may directly be regarded as rustless.

In the production of such rustless iron it has been found particularly suitable to use lime-white as an adhesive, either in the iron ore charge or in the chromium ore charge, or in both kinds of charge. The reason for this is that the chromium ores contain, as a rule, a large quantity of magnesia, which makes the slag produced viscous unless a comparatively large quantity of lime is added. By the addition of lime-white, an almost complete desulphurization of the metals is obtained at the same time while reducing and melting the charges of the two kinds of ore, inasmuch as the lime covering the grains as a film absorbs the sulphur while forming sulphide of calcium which is absorbed in the slag.

In order to form a suitable slag in the furnace for the reduction and the melting of the different kinds of charge, requisite fluxes may be admixed either in a finely divided state in preparing the different kinds of charge, or such fluxes may be directly introduced into the furnace. Preferably, the admixture of flux is then adapted so that a slag is obtained which is suited to each separate reduction process.

The following is a specific example of the proportioning of the charges in accordance with our invention for the production of so-called rustless iron, it being understood, however, that the invention is not limited to the composition of the different charges referred to herein.

For the production of rustless iron, an iron charge and a chromium charge are used having the following composition in part by weight:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Iron charge</th>
<th>Chromium charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Charcoal</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Lime</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Chromium ore</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>Charcoal</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Lime</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Quartz</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The charges are both prepared of finely divided ore, preferably of such a grading as to be able to pass a sieve having at least 850 meshes per cm.² and finely divided charcoal of the same grading. The lime is preferably used in the form of lime-white and acts as a binding agent. After the materials have been accurately mixed and the mixture brought into briquettes or other pieces, the charges are carefully dried. The iron charge is then fed into the electric furnace and reduced and melted whilst floating on or in a slag bath in the same way, at least in part, of electric resistance heat developed in said slag bath, an iron very low in carbon being then obtained on the bottom of the furnace, whereas the slag becomes rather rich in ferrous oxide. The greater part of the slag is then tapped off and the slag may be deoxidized, for instance by introducing into the furnace briquettes or other bodies of manganese ore and carbonous material, for the purpose of saving chromium. The chromium charge is then fed into the furnace and reduced and melted in the same manner as the iron charge. In order to utilize chromium oxide contained in the slag, a suitable quantity of a thermal reducing agent, preferably ferro-silicon, may be added to the slag. By suitably adapting the quantity of the chromium charge, an iron having the content of chromium desired will be directly obtained.

If, on the other hand, stainless steel is to be produced, the carbon content in one of the charges should be suitably proportioned so as to obtain a chromium steel having the intended contents of chromium and carbon.

What we claim is:

1. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent or constituents, which, in a group of steps, includes forming separate mixtures of each of said ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures separately, and reducing and melting said briquettes on a slag bath in an electric fur-
nace whilst proportioning the quantity of briquettes of each kind so as to obtain an alloy of the desired composition.

2. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent or constituents, which, in a group of steps, includes forming separate mixtures of each of said ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures separately and reducing and melting on a slag bath in an electric furnace whilst proportioning the quantity of briquettes of each kind in order to provide the exact percentage of metal contents in the final product.

3. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent or constituents, which, in a group of steps, includes forming separate mixtures of each of said ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures separately, reducing and melting said briquettes on a slag bath in an electric furnace whilst proportioning the quantity of briquettes of each kind in order to produce an alloy of the desired composition.

4. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent, which, in a group of steps, includes forming separate mixtures of each of said two ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures separately, reducing and melting said briquettes on a slag bath in an electric furnace whilst proportioning the quantity of briquettes of each kind in order to produce an alloy of the desired composition.

5. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent, which, in a group of steps, includes forming separate mixtures of each of said two ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures separately, reducing and melting said briquettes on a slag bath in an electric furnace whilst proportioning the quantity of briquettes of each kind in order to produce an alloy of the desired composition.

6. A method of producing an alloy of a metal belonging to the iron group directly from oxide ore of said metal and oxide ore of the alloy constituent or constituents, which, in a group of steps, includes forming separate mixtures of each of said two ores with an amount of carbon-containing reducing agent proportioned to the reduction of the ore and to the desired percentage of carbon in the alloy obtained therefrom, briquetting said mixtures respectively, reducing and melting said briquettes on a slag bath in an electric furnace whilst proportioning the quantity of briquettes of each kind in order to produce an alloy of the desired composition.