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MANUFACTURE OF ALLOY STEELS.

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This application is a continuation in part of my copending application, Serial No. 543,082, filed March 11, 1922.

The present invention relates to manufacture of alloy steels, and more particularly to the reduction of the alloying elements directly from their ores, and the production of the respective allow steels, without the introduction of excess carbon in the finished steel.

The process of the present invention is particularly applicable to the making of chrome steel, whereby the major portion, if not all, of the chromium is introduced into the steel by its direct reduction from an unreduced chromium compound, such as chrome ore, added to the bath in the steel-making furnace.

In the manufacture of alloy steels, under the practice heretofore prevalent, the alloying elements, in the already reduced metallic state, mostly in the form of a ferro-alloy, are added to a molten bath of steel. For example, to obtain the respective steels thereof, ferro-manganese, ferro-chromium, ferro-titanium, ferro-tungsten, ferro-vanadium, ferro-uranium, ferro-molybdenum, ferro-nickel or metallic nickel and ferro-cobalt or cobalt metal, are added to steel, in the molten state in the furnace, or after it is tapped in the ladle. As the regular commercial grades of such ferro-alloys contain an appreciable amount of carbon, this practice introduces an undue amount of carbon in the steel. If special grades of low-carbon ferro-alloys are used, the cost of such alloys is comparatively so high as to prohibitively increase the cost of steel produced. These defects are especially apparent in the case of steels where the content of the alloying element has to be high and the carbon content low, as in the case of the so-called "stainless" steels, which have a chromium content of between 9 and 15% and a low carbon content.

It is not commercially practicable to use the regular high carbon ferro-alloys, and then decarbonize the steel after their addition, as the process of oxidizing the carbon is accompanied by an oxidation, and consequent waste, of the valuable alloying elements.

Another deficiency of the existing methods of manufacturing alloy steels, by the addition of metallic ferro-alloys to molten steel, is the phenomenon of segregation. The alloy being added in the solid state in the form of lumps scattered over the surface of the molten steel, causes points of concentration of the alloying element at the location of each of the lumps. As the steel is tapped immediately after melting of the lumps in order to avoid an undue oxidation of the alloying element, these points of higher concentration have no opportunity to equalize themselves over the entire mass of metal by diffusion. Moreover, the ferro-alloys have various constituents of different melting points and degrees of solubility, as for example the carbides in the ordinary grades of alloy. Such carbides have a higher melting point than the remainder of the alloy. Such a carbide-containing ferro-alloy, when added to molten steel, will have the result that when the rest of the alloy will be completely assimilated, the carbide content will still be in the solid state, floating in the molten steel, without giving up its alloying element content to the bath. Such solid particles with a high alloying element content will persist in the steel on solidification and present segregations.

I overcome the above mentioned difficulties by adding the alloying element to the bath in the form of the oxide or ore and reducing it with a reducing agent contained in the molten steel. The reducing agent and the alloying material are added separately. This permits the reducing agent, as for example, silicon, to be incorporated into the metal bath unmixed with the alloying material, and permits the alloying material, as for example, chrome ore, to be incorporated into the slag unmixed with the reducing agent. The reducing agent and alloying material can therefore each become disseminated through its own layer of the bath, and the reaction between them will then take place at the contact surface between the metal and slag layers. Moreover, the separate addition of the reducing agent and the alloying material permits one to be added prior to the other. It is preferred to add either the reducing agent or the alloying material long enough prior to the addition of the other, so that the one first added may have an opportunity to be disseminated before the addition of the other. For example, if the alloying ore such as chromite is added first, it will become disseminated throughout the slag layer, and as it is in the oxide form the chromium cannot be burned

during the dissemination time. Or if the reducing agent, such for example as silicon, is added first, it can become disseminated through the steel layer before the alloying ore is thrown onto the slag. When the alloying ore is thrown onto the slag layer it becomes diffused in it and meets the reducing agent at the surface of contact between the slag and steel, the reaction taking place over the entire contact surface. The reduced alloying metal in its nascent state is in contact with steel bath, and therefore the best conditions are obtained for the alloying and uniform disseminating of the alloying metal throughout the steel. The alloying element is obtained from a cheap source. The introduction of carbon and segregation are avoided in the finished steel.

The action of the alloying oxide or ore in oxidizing the reducing agent in the steel and action of the added fluxing material, generally lime, in absorbing and neutralizing the oxidized reducing agent together with undesirable metalloids, such as phosphorous and sulphur, causes a refining of the steel to take place simultaneously with the production of the alloy.

The process may be carried out in the following manner:—

The steel, to which the alloying element is to be added, is first brought to a molten condition, in an ordinary steel making furnace, such as an open-hearth furnace, electric furnace, or other suitable furnace. Next, the reducing agent, which may be a carbonaceous material, for instance in the form of metal carbide, such as pig iron, or wash metal, or which may be a so called metallic reducing agent, such as silicon or its alloys, such as ferro-silicon, manganese, calcium, magnesium, or the like or their alloys, is added to the bath of molten steel and sufficient time allowed for its complete assimilation through the body of the molten metal. These so called "metallic" reducing agents have an exothermic reaction with the oxides of the alloying metals and may therefore be referred to as exothermic reducing agents.

The ferro-alloys of the reducing agents, and particularly ferro-silicon, have sufficient specific gravities, such that they usually sink immediately through the slag layer to the metal layer. However, the physical condition, such as the size of the pieces, may influence the readiness with which these ferro-alloys pass through the slag layer. In case the pieces are relatively fine, they may float on the slag in spite of their greater specific gravity until they melt and trickle through the molten slag to the metal layer. The relatively pure reducing agents have, however, smaller specific gravities than their ferro-alloys, and consequently, may not become incorporated into the metal layer until after they have become molten. In order to facilitate the sinking of the reducing agent through the slag layer, the fluidity of the slag layer may be controlled by the proper selection of fluxing materials.

The quantity of this reducing agent added is figured sufficient to reduce the required percentage of the alloying element from the raw material containing it to be added in the next step of the process. The alloying raw material in the right proportion or in slight excess is then added, preferably in the presence of lime, or lime, fluor-spar and borax as a flux. The purpose and function of the flux is to produce a slag with the gangue of the raw material containing the alloying element, and is of such a nature as to effectively remove by chemical combination the product formed by oxidation of the reducing agent, for example, in the case of chromite which is in its natural state highly refractory and chemically inert, the flux combines with the gangue, (which consists principally of silica, alumina and magnesia) to form a molten slag leaving the chromium and iron oxides in a condition amenable to reduction. The slag containing the fluxing material is capable of absorbing the silica produced by the oxidation of the silicon content of the metal bath when silicon is employed as the reducing agent. The practical result achieved by the flux, therefore, is the removal of the presence of the reducing agent in the finished steel. For example, a lime flux combines with and neutralizes the silicon oxide formed when silicon is the reducing agent. The specific gravity of the raw alloying material is such that it remains in the slag layer. This raw material and flux combining at the temperature of the furnace form a supernatent, non-metallic, liquid layer over the molten body of metallic steel and in contact with it. The reducing reaction then proceeds at the surface of contact of the non-metallic and metallic liquid bodies. At the end of this reaction period the temperature in the furnace may be raised, in the case of an electric furnace, for instance, by increasing the current density and voltage, in order to eliminate the last traces of the reducing agent in the finished steel, accelerating the effect produced by the fluxing agents added for this purpose.

At the ordinary refining temperatures, the silicon and chromium are more readily oxidized than carbon, and the carbon is therefore difficult to eliminate. However, when the temperature is increased, as above described, the speed of reaction between oxygen and carbon is increased relatively more than the speeds of reaction between oxygen and silicon and oxygen and chromium, so that the effect of increasing the furnace temperature before tapping is to cause an elimi-

nation of the carbon relatively greater than that of silicon and chromium. This is of particular importance in the production of very low carbon chrome steels or irons. The ordinary refining temperatures are about from 1500 to 1600 degrees C. for an electric furnace or 1400 to 1500 degrees C. for a fuel heated open hearth furnace. The temperature increase above described is usually from about 50 to 250 degrees above the usual refining temperatures. In the case of carbon which, of course, is always a reducing agent, the increase in temperature will eliminate it down to .1 to .06% or even lower. Where there are two reducing agents present, such as carbon and silicon, the increased temperature will eliminate both of them, the carbon to .1 to .06%, and the silicon to about the same degree.

In general it is preferred to add the reducing agent to the molten steel first, then adding the raw material containing the alloying element. The tolerance limits in the finished steel of elements such as carbon or silicon, forming the reducing agent, are usually much narrower than the tolerance limits of the alloying element, and by introducing the reducing agent first, limits may be accurately controlled by successive additions of raw alloying material until the presence of the reducing agent is eliminated to the desired extent. On the other hand, if the tolerance limits for the alloying element are narrow, the order of procedure may be reversed, and the raw alloying element containing material may be charged first together with the flux, and the reducing agent charged then in successive portions, until the desired limit of alloying is effected.

While it is usually preferred to first form the molten bath by melting down the charge so as to form the steel layer and slag layer and then to add the reducing agent and unreduced ore to the respective layers, it will be obvious that the reducing agent and ore may be otherwise incorporated into their respective layers of the bath. For example, the reducing agent, such as a silicon reducing agent, may be introduced into the furnace along with the unmelted charge, so that the reducing agent becomes incorporated into the metal layer along with the melting charge. Similarly, a portion, or perhaps all of the ore, may be added to the furnace along with unmelted charge materials, and because of its specific gravity will become incorporated into the slag layer upon the melting of the charge materials.

The most generally adopted metallic reducing agent is ferro-silicon. However, silicon metal or any other silicon alloy such as a silicon alloy containing one of the alloying metals may also be advantageously used. For instance, in the case of the manufacture of so-called "stainless" steel a silico-chromium alloy may be incorporated in the molten steel and its silicon content utilized to reduce a further quantity of chromium from chrome ore added to the bath. This procedure is especially advantageous in the case of a steel containing a high percentage of the alloying element.

In the case of alloy steels containing a plurality of alloying elements, this procedure may be carried out in the same manner, the raw materials in the right proportions, containing the plural alloying elements, being charged together on top of the molten bath of steel containing the reducing agent. In such cases a flux may be separately added or the raw alloying materials may be selected of such composition as to have in their gangue the necessary fluxing components.

Also a plurality of reducing agents may be used such as a mixture of carbonaceous and metallic reducing agents or several different metallic reducing agents. For instance a ferro-silicon alloy containing carbon may be used, both its silicon and carbon contents being utilized for the reduction purpose. Also any reducing agents originally present in the steel bath may be effectively used, in which case during the reduction operation. a simultaneous refining of the original steel will take place. Also the fluxes added with the alloying-element-containing raw material will have the secondary effect of refining the steel of the metalloid contents such as sulphur and phosphorus simultaneously with the reducing operation.

If desired, after reduction of the alloying element or elements in the steel, a small quantity of additional ferro-silicon or ferro-manganese may be added as a deoxidizing cleanser, before tapping, as is the common practice in making alloy steels.

The advantages of this process of alloying are especially marked in the case of using silicon as a reducing agent, and producing chrome steels with a high alloy content and very low carbon content. As such an instance may be cited the manufacture of so-called "stainless" iron containing 9 to 15% chromium and less than 0.1% carbon. Also the advantages of this process are apparent in the case of alloying a highly oxidizable and difficultly soluble element as uranium in steel. The alloying element being produced in the nascent state and directly in contact with the steel, the chances of its oxidizing or not dissolving are reduced to a minimum. Also, as the carbon content of the finished steel can be eliminated to any desired extent, simultaneously during the process of reducing, the exact percentage of carbon in the finished alloy steel can be arrived at more accurately by recarburizing before tapping. In the case of metallic reducing agents being used their presence in the finished steel is

practically eliminated by the action of fluxes. Thus by the process of this invention a steel of predetermined given composition can be more accurately produced than by the use of ferro-alloys. Also by this process, as the valuable alloying elements do not exist at any time in the metallic state, unless dissolved and alloyed in the steel itself, and as after their solution in the steel there is no occasion to subject such steel to an oxidizing process for removal of carbon, for instance, as in the older processes, there is no loss suffered through oxidation, rendering the process extremely economical.

While certain features of the present process, and particularly the substantial elimination of the reducing agents by increasing the final furnace temperature, are novel and useful in the manufacture of various alloy steels, the present invention is particularly applicable to the production of chrome steel in which a substantial quantity of chromium is introduced into the steel. The chromium content is furnished principally, if not entirely, by the chrome ore which is charged into the slag layer and which reacts with the silicon reducing agent in the metal layer to thereby directly reduce the chromium from the ore to the metallic state in the bath of the steel-making furnace. While the chromium ore charged into the slag is contemplated as being the principal, if not the entire, source of the chromium, minor proportions of chromium may be introduced by some of the other constituents added to the bath.

As above pointed out, the chromium is supplied from a very cheap source, and the necessity of employing a relatively expensive chromium alloy as the source of chromium is obviated. Moreover, the treatment permits the production of a low carbon chrome steel and when desired, also a low silicon chrome steel.

The term "steel" as herein employed is intended as a term of general description and not of limitation, and is intended to include the so-called "stainless irons" which are, in reality, steels having very low carbon and metalloid contents. The term "chrome steel" is also intended as a term of general description, and not of limitation, and is intended to include steels having chromium as the principal alloying metal, although containing other alloying metals.

The expression "silicon reducing agent" is intended as a term of general description and not of limitation, and is intended to include not only substantially pure silicon, but also alloys of silicon with other metals or metalloids.

The silicon and chrome ore may be in whole or in part incorporated into their respective layers of the bath, either before or during the maintenance of the reaction temperature in the furnace, and I therefore do not intend to limit my claims, except when specifically stated therein, to any particular sequence of steps of incorporating the reducing agents, and unreduced compounds and the maintenance of the reacting temperature.

While my process is particularly applicable to the production of chrome steel, it may be employed in the production of alloy steels in general and especially to steels containing an alloying metallic element of the sixth group of the periodic system, such metallic elements being chromium, molybdenum, tungsten and uranium.

While the preferred method of carrying out my process has been specifically described, it is to be understood that the invention is not limited to all of the described details, but may be otherwise embodied in processes of making alloy steels, within the scope of the following claims.

I claim:

1. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer in which is incorporated a silicon reducing agent and a slag layer in which is incorporated an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

2. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer in which are incorporated silicon and carbonaceous reducing agents and a slag layer in which is incorporated an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agents in the metal layer and the unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

3. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer in which is incorporated a silicon reducing agent and a slag layer in which is incorporated an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel and a fluxing material which removes by chemical combination the silica produced by the oxidation of the silicon together with objectionable metalloids such as sulphur and phosphorous, and maintaining the bath at a tem-

perature sufficient to cause a reaction between the reducing agent in the metal layer and unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound and simultaneously refine the steel, substantially as described.

4. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer and a supernatant slag layer, adding to the bath a silicon reducing agent of such specific gravity that it sinks through the slag layer into the metal layer and an unreduced chromium compound of such specific gravity that it remains in the slag layer, the chromium compound being in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent and the unreduced chromium compound to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

5. The process of making chrome steel, comprising forming a bath of steel having a metal layer and a supernatant slag layer, adding separately to the metal layer a silicon reducing agent and to the slag layer an unreduced chromium content in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, and allowing sufficient time between to permit the one first added to become disseminated whereby segregation of the chromium is avoided, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

6. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer and a supernatant slag layer, and adding separately to the metal layer a reducing agent and to the slag layer an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, the one containing the element whose percentage is to be most accurately controlled in the finished steel being added first, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

7. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer in which is incorporated a silicon reducing agent and a supernatant slag layer, thereafter adding to the slag layer an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced chromium compound in the slag layer to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

8. The process of making chrome steel containing other alloying metals, comprising forming a molten bath of steel having a metal layer in which is incorporated a silicon reducing agent and a slag layer in which are incorporated unreduced compounds of chromium and the other alloying metal or metals in amounts sufficient to furnish the major portion, if not all, of the alloying metal contents of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and unreduced alloying metal compounds in the slag layer to thereby reduce in the bath the alloying metals directly from their unreduced compounds, substantially as described.

9. The process of making alloy steel, comprising forming a molten bath of steel having a metal layer in which is incorporated a reducing agent and a slag layer in which is incorporated an unreduced compound of the alloying metal, maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced compound of the alloying metal in the slag layer to thereby directly reduce the alloying metal in the bath, and finally increasing the temperature sufficiently to substantially eliminate any reducing agents from the finished steel, substantially as described.

10. The process of making an alloy steel containing as an alloying metal a metallic element of the sixth group of the periodic system, comprising forming a molten bath of steel having a metal layer in which is incorporated a silicon reducing agent and a slag layer in which is incorporated an unreduced compound of the alloying metal in an amount sufficient to furnish the major portion, if not all, of the said alloying metal content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced alloying metal compound in the slag layer, to thereby reduce in the bath the alloying metal directly from its unreduced compound, substantially as described.

11. The process of making an alloy steel containing as an alloying metal a metallic element of the sixth group of the periodic system, comprising forming a molten bath of steel having a metal layer in which is in-

corporated a reducing agent and a slag layer in which is incorporated an unreduced compound of the alloying metal in an amount sufficient to furnish the major portion, if not all, of the said alloying metal content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced alloying metal compound in the slag layer, to thereby reduce in the bath the alloying metal directly from its unreduced compound, substantially as described.

12. The process of making an alloy steel containing as an alloying metal a metallic element of the sixth group of the periodic system, comprising forming a molten bath of steel having a metal layer containing a reducing agent and a supernatant slag layer, thereafter adding to the slag layer an unreduced compound of the alloying metal in an amount sufficient to furnish the major portion, if not all, of the said alloying metal content of the steel, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent of the metal layer and the unreduced compound in the slag layer, to thereby reduce in the bath the alloying metal directly from its unreduced compound, substantially as described.

13. The process of making chrome steel, comprising forming a molten bath of steel having a metal layer and a slag layer in which slag layer is incorporated an unreduced chromium compound in an amount sufficient to furnish the major portion, if not all, of the chromium content of the steel, thereafter adding a silicon reducing agent to the metal layer, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced chromium compound in the slag layer, to thereby reduce in the bath chromium directly from its unreduced compound, substantially as described.

14. The process of making an alloy steel containing as an alloying metal a metallic element of the sixth group of the periodic system, comprising forming a molten bath of steel having a metal layer and a slag layer in which slag layer is incorporated an unreduced compound of the alloying metal in an amount sufficient to furnish the major portion, if not all, of the said alloying metal content of the steel, thereafter adding a reducing agent to the metal layer, and maintaining the bath at a temperature sufficient to cause a reaction between the reducing agent in the metal layer and the unreduced compound in the slag layer, to thereby reduce in the bath the alloying metal directly from its unreduced compound, substantially as described.

In testimony whereof I have hereunto set my hand.

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