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PROCESS OF PRODUCING ALLOYS

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This invention relates to the production of ferrous alloys and more particularly the production of alloy irons and steels, especially corrosion-resistant irons and steels, wherein the alloy metal is directly reduced from the reducible oxides thereof.

Among the objects of my invention is the production in a simple, efficient and thoroughly practical manner of alloy steels of desired characteristics such as strength, ductility, corrosion resistance, electrical resistance, magnetic permeability and the like made to a desired specification of alloy content such as chromium, nickel, vanadium, silicon, which are consistently sound in the ingot and which are free from rising or swelling in the mold.

The invention accordingly consists in the several steps and in the relation of each of the same to one or more of the others as described herein and the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of certain features of my invention it may at this point be noted that in the production of metals high in alloy content by means of direct reduction processes, as for example in the production of corrosion-resistant irons and steels (irons and steels containing chromium in the amount of from about 10% to 30%, with or without nickel and other alloying ingredients) or in the production of these same alloy irons and steels by the usual method of employing ferro-alloys, or in the production of high silicon iron such as transformer iron, or even in the production of ordinary steels, such as chrome-nickel, chrome vanadium and the like, it is not uncommon to encounter a deleterious gaseous condition evidenced by failure of the metal to shrink properly in the molds, or even by swelling or rising of the metal in the molds. The resultant formation of blow holes in the solidified steel renders it of distinctly inferior quality, and useless for most purposes. Apparently the use of considerable quantities of silicon as a deoxidizer or alloying agent, but especially as a reducing agent in direct reduction processes for the manufacture of alloy iron and steels, intensifies this gaseous condition.

While various attempts at explanation of this peculiarity have been advanced, such as casting at too high a temperature, over-reduction or over-oxidation, none of these explanations afford a complete solution of the above-mentioned objectionable conditions and consistently permit the production of sound metal.

One of the outstanding objects of this invention is the consistent production of sound, gas-free ferrous alloys and alloy irons and steels, especially corrosion-resistant or stainless irons and steels, in a simple, reliable and economical manner from readily available and inexpensive raw materials and employing well-known processing equipment.

Referring now more particularly to the practice of my invention, in the manufacture of ferrous alloys especially when the alloy content is obtained by a direct reduction of reducible oxides of the alloy metal, the raw materials employed, such as the reducible oxides, the oxidizing and reducing agents, the slag forming ingredients and to a lesser extent whatever metallic scrap is employed as well as the furnace refractories used, contain various amounts of moisture in a free and/or combined state. This moisture is introduced into the furnace along with the raw materials and furnace refractories during the practice of the process as will appear more fully hereinafter. Under the action of intense and prolonged heat of the furnace and/or the mild pressure conditions existing therein, the moisture contained in the raw materials comes out of these materials and is disassociated with the consequent liberation of free oxygen and free hydrogen. The release of moisture from the raw materials and the disassociation of this moisture into the component elements oxygen and hydrogen becomes of considerable consequence when the electric arc furnace is employed; intense heat produced therein and the peculiar characteristics of the electric arc are particularly potent factors in the dissociation of chemical compounds.

Upon dissociation of moisture, the resultant oxygen combines readily with the components of slag and metal, leaving the hydrogen free and in a very active state. This hydrogen is readily soluble in slag and metal, and is absorbed therein especially if there is any degree of moderate pressure in the furnace. The activity and tendency of the hydrogen to enter slag and metal appears to be heightened by the presence of silicon, especially in direct reduction processes where considerable amounts of silicon are present. When hydrogen gas becomes dissolved in the metal it is exceedingly difficult to remove this gas until the metal solidifies. When the heat of metal is poured into ingot molds and allowed to solidify and cool the hydrogen comes out of solution and forms blowholes in the solidified metal which render it unsound and unsuitable for use.

To prevent the metal bath from absorbing gases evolved during the production of a heat of ferrous alloy metal and thus preclude the fatal formation of blowholes in the metal during solidification and the objectionable rising and swelling of the metal in the molds causing unsound metal of little commercial use, in accordance with the provisions of my invention a portion of the reducing agent, deoxidizer, alloying agent or the like, is preferably replaced by a reagent which in addition to aiding in the reduction, deoxidation, alloying or like operations, combines with gas

evolved during the operation of the process, all as more particularly described above, to effectively remove contaminating gas as it is formed.

In, for example, a direct reduction process for producing corrosion resisting or stainless chromium or chromium-nickel irons and steels, the ore of the desired alloying element, such as chrome ore, is added to the furnace after mixing thoroughly with a suitable reducing agent such as ferro-silicon. Frequently in such a direct reduction process there may be an excess of reducible oxide, although the proportions of reducible oxide to reducing agent may vary from an excess of one to an excess of the other. In any proportion which may be employed, there is a considerable volume of raw materials charged into the furnace, all of which may contain moisture either as free moisture or combined moisture or both. All of such moisture tends to dissociate wholly or in part, thus permitting the absorption of hydrogen by the metal. This is particularly true of the electric arc furnace. In addition, there is the tendency of the silicon itself to promote the absorption by the metal of hydrogen.

When a suitable reagent such as an alloy of silicon and calcium, commercially called calcium silicide or calcium silicon, which contains 20 to 35% calcium and 50 to 70% silicon, the balance being chiefly iron, is wholly or in part substituted for the ferro-silicon employed in these processes, any free hydrogen present in the process will be effectively combined with the calcium silicon on dissociation of the latter, to form hydrides which are automatically removed from the process. Considerable carbon is frequently present in commercial calcium silicon, but the percentage of carbon in the calcium silicon substituted for the ferro-silicon should be low so that an undesirable increase of carbon content in the metal will not result from this substitution.

In accordance with the provisions of my invention calcium silicon is substituted for a part of the ferrosilicon reducing agent in an amount by weight of from 10 percent to 100 percent of the ferro-silicon reducing agent ordinarily employed. Best results are obtained, however, when the amount of calcium silicon utilized approximates about one-fourth of the total weight of the silicon ordinarily employed as ferro-silicon. For example, in a process wherein a total of about 2500 pounds of 50% ferro-silicon is ordinarily employed, 25% by weight of the contained silicon, or approximately 312 pounds of silicon may be added as calcium silicon in substitution for an equal amount by weight of silicon as ferro-silicon (625 pounds of ferro-silicon). Thus, in this instance, instead of employing the total of 2500 pounds of 50% ferro-silicon in the process, there is preferably employed as a reducing agent 1875 pounds of ferro-silicon together with an amount of calcium silicon sufficient to make up the silicon deficiency, or illustratively, 625 pounds of calcium silicon analyzing 50% silicon. The proportions of calcium silicon to ferro-silicon may be varied, however, within the range heretofore given, the particular amount of calcium silicon employed being largely dependent upon the extent of moisture dissociation going on within the furnace.

When larger quantities of moisture is dissociated, due for example to high moisture content of the raw materials, or to conditions within the furnace especially fostering moisture dissociation, greater proportions of a reducing reagent having the property of combining with the hydrogen gas produced, as more particularly described above, are preferably used. And similarly, when little moisture dissociation accompanies the practice of the process less quantities of the reduction agent are found adequate in the prevention of gas absorption by the metal.

In employing a reducing agent which combines with the evolved gas, best results are obtained when this reducing agent, illustratively calcium silicon, is thoroughly mixed with the other reducing agent employed, such as ferro-silicon, as well as with the reducible oxide and the desired slag forming ingredient.

When calcium silicon is used as a deoxidizer or alloying agent, maximum benefit from it in preventing absorption of hydrogen is achieved during the time it takes to fuse the calcium silicon. During this period, when used alone or in combination with other deoxidizers or alloys, calcium silicon is highly effective in preventing the hydrogen absorption of the metal.

When the mixture of ferro-silicon, reducible ore and calcium silicon is charged into the furnace wherein the desired temperature conditions prevail, the usual reaction occurs between the ferro-silicon and ore, whereby the latter is reduced. This reaction is aided to some extent by the presence of the calcium silicon, although as has previously been pointed out, the chief advantage in its use lies in its dissociable characteristics, whereby calcium is liberated for effective combination with the free hydrogen present in the furnace, resulting in the formation of hydrides, which do not dissolve in or become absorbed by the metal. Thus, since the free hydrogen combines with the liberated calcium, hydrogen is thereby prevented from becoming absorbed by the metal bath to contaminate the same. A process is thus provided wherein the gaseous content of the metal produced is minimized and blowholes are prevented from forming in the finished solidified product.

In addition, a further advantage is derived from the use of the calcium silicon, in that the liberated calcium aids in holding phosphorus present in the process in retention in the slag, so that contamination of the bath with phosphorus is somewhat reduced.

In addition to these many practical benefits, calcium silicon or calcium silicide is highly effective in lending a certain fluidity to the slag of chrome ore, reducing agent and lime overlying the bath of metal. The fluid condition of the slag permits a smoother and more uniform action of the furnace electrodes in the operation of the furnace with a consequent minimum dipping of electrodes into slag and metal, thereby assuring minimum carbon contamination of the ferrous metal bath.

The use of calcium silicon as a substantial part of the reducing agent employed, effects a perceptible decrease in the silicon contamination of the bath of metal. This highly desirable result is achieved because of the lower density of this material, as compared with ferrosilicon, and the consequent decreased tendency for the agent to gravitate into the metal bath and directly alloy the bath with silicon.

As illustrative of the practice of my invention in, for example, the production of a corrosion resisting alloy iron of about 17% chromium and less than 0.10% carbon, after the initial melt-down of about 4000 pounds of steel scrap and about 100 pounds of iron ore to form a bath of ferrous metal, the reduction period is commenced. For the production of a low carbon chromium-iron

stainless alloy, a charge of about 10,000 pounds of chrome ore, 1800 pounds of 50% ferro-silicon and about 500 pounds of calcium silicon is intimately mixed, separated into batches, and each batch successively charged into the furnace. The chrome ore is reduced, the resulting metal directly entering the ferrous metal bath. Upon completion of the reduction period whereby sufficient chrome is reduced from the chrome ore, the resulting slag is removed and the finishing period is commenced. In finishing the heat of metal about 400 pounds of calcined lime is fused to form a new slag, and about 50 pounds of low carbon ferro-manganese is added to the bath to deoxidize contained oxides dispersed throughout the molten metal. The molten metal is then tapped into a ladle from which it is poured into suitable molds, where it is permitted to cool and solidify. The metal solidifies without the highly objectionable rising or swelling in the molds and the solid metal is entirely lacking in perceptible gaseous content or objectionable blowholes.

Thus it will be seen that there is provided in this invention a process of producing sound gas-free ferrous alloy metal in which the various objects hereinbefore noted, together with many thoroughly practical advantages, are successfully achieved. It will be seen that the process is simple, practical, and economical and that it lends itself to consistent production of a variety of sound ferrous alloys.

While as illustrative of the practice of my invention the reagent, calcium silicide is employed to effect a combination with hydrogen gas normally produced as a result of the electric arc furnace dissociation of moisture evolved during the reduction of ores of alloying elements, thereby assuring the production of sound, gas-free alloy irons and steels, good results are achieved where appropriate quantities of one or more of calcium hypochlorite, potassium chloride or calcium chloride are added to the ore and/or reducing agent, as more particularly indicated in my copending application Ser. No. 557,372, filed August 15, 1931 and entitled Process of producing alloys. Where these reagents are employed the amount used is over and above the amount of reducing agent required to effect the desired reduction of the ore. It will be understood that one or more of the ingredients, calcium hypochlorite, potassium chloride or calcium chloride, with or without calcium silicide, may be employed as desired to assure the production of sound, gas-free metal.

As many possible embodiments may be made of my invention and many changes made in the embodiment hereinbefore set forth it will be understood that all matter described herein is to be interpreted as illustrative, and not in a limiting sense.

What I claim is:

1. In the production of corrosion resistant irons and steels, the art which includes, preparing a bath of ferrous metal, and adding to said bath chrome ore and a reducing agent including an agent having the functional characteristics of calcium silicide whereby the reduction product combines with hydrogen gas evolved during the practice of the process thereby assuring the production of gas-free metal.

2. In the production of alloy irons and steels of high alloy contents, the art which includes, preparing a bath of ferrous metal, and charging onto said bath a mixture of reducible oxide of an alloy metal and a reducing agent comprising ferro-silicon and calcium silicide in proportions of about three to one whereby said oxide is reduced, the alloy metal entering the bath, and hydrogen evolved during the operation of the process reacts with the calcium released during the reduction of the oxide to prevent the evolved hydrogen dissolving in the bath of metal.

3. In the production of a corrosion-resistant iron or steel, the art which includes, preparing a bath of ferrous metal, and adding to said bath chrome ore together with a reducing agent therefor including calcium silicide whereby said ore is reduced and hydrogen evolved during the reduction of said ore combines with a part of the product of said reduction to prevent the solution of said hydrogen in the metal.

4. In the production of a corrosion resistant iron or steel, the art which includes, preparing a bath of ferrous metal, and adding to said bath chrome ore together with calcined lime, ferro-silicon and calcium silicide in such proportions that the chrome ore is reduced and a portion of the reduction product combines with hydrogen evolved during the process to prevent such hydrogen dissolving in the bath of metal.

5. In the production of a corrosion-resistant iron or steel, the art which includes, preparing a bath of ferrous metal, adding chrome ore to said bath, and adding a reducing agent comprising a silicon-containing agent and calcium silicide in the proportion of about three to one for the respective silicon contents thereof whereby said ore is reduced and the calcium released by said reduction combines with hydrogen gas evolved during the practice of said process thereby precluding the absorption of said gas by said bath of metal.

6. In a process for the production of corrosion-resistant irons and steels by means of the direct reduction of chrome ore by a reducing agent in the presence of a molten bath of iron or steel, the improvement which comprises mixing with the ore and the free and combined moisture in the ore and reducing agent a reagent of such character as to combine with hydrogen evolved during the dissociation of said moisture in the practice of said process, whereby the amount of hydrogen absorbed by said bath is maintained below the quantity which will remain in solution at the solidification point of said iron and steel thereby assuring the production of sound metal free of blowholes.

7. In the production of corrosion-resistant irons and steels, the art which includes, reducing chrome ore containing a normal amount of free and combined moisture in the presence of a molten bath of iron or steel and in the presence of a reagent mixed with said ore and a reducing agent employed in the reduction of the ore, said reagent being of such character as to combine with hydrogen liberated during the dissociation of the moisture evolved from the ore and reducing agent in the practice of the process, thereby assuring the production of sound, gas-free metal.

8. In the production of corrosion-resistant irons and steels, the art which includes, preparing a bath of ferrous metal, and adding to said bath chrome ore and a reducing agent therefor comprising ferrosilicon and calcium silicide in proportions of about three to one for the respective silicon contents thereof.

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