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ALLOYS

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The invention relates to the production and manufacture of iron-chromium alloys low in carbon or substantially free from carbon and having the characteristic property that they are non-stainable or rustless alloys under weather exposure or when treated with certain weak acids. Typical examples of such chromium iron alloys are those with a chromium content of from 9 to 16% or more of chromium and a carbon content of about 0.4% more or less. When such alloys have a very low carbon content such as 0.1% or under they are ductile and malleable, and these physical properties render them readily workable, thereby enlarging their usefulness for the preparation of a great variety of manufactured articles.

Similar chromium-iron alloys are known containing a proportion of nickel.

Hitherto, these chromium-iron alloys with or without a proportion of nickel, have been manufactured by adding the chromium in the form of refined or substantially carbon-free ferro-chrome, which is dissolved in the requisite proportion of steel in an electric furnace.

The object of my invention is to prepare and manufacture iron-chromium alloys of the kind referred to by the direct use of molten steel and so as to produce an alloy which shall be free or substantially low in carbon, the reagents employed being such that any impurities which may be introduced into the alloy steel thus prepared are readily removable subsequently without incurring losses by oxidation of the contained chromium.

According to the invention stainless or rustless iron chromium alloys low in carbon or substantially free from carbon and of the character described are produced or manufactured by a process comprising or including the addition to molten steel of a thermo-reaction mixture comprising or containing a reducible ore or other appropriate compound of chromium, such as chromite, and silicon, or a silicon alloy, free or substantially free from carbon.

The invention also includes the use of a refining operation for the oxidation of the silicon in the molten iron-chromium alloy so produced. This refining operation may be effected by the use of a gaseous oxidizing medium, and/or by the use of solid ingredients.

As the reducible compound of chromium, cleaned chromite is preferably employed, and as reducing agents I employ silicon and the silicon alloys of calcium, magnesium, iron and/or aluminium. With any or all of these silicon-containing reducing agents may be employed a proportion of a more powerful reducing agent such as granulated aluminium or a calcium alloy.

The invention also includes the use of a chromium-silicon alloy either as the reducing agent or as a constituent thereof, and as ingredients used in the production of the iron chromium alloy chromium, chromium alloys, nickel and/or nickel alloys may also be employed.

The invention also includes the use of a converter or other container or furnace for the alloying and/or refining operation, and the use of the thermo-reaction mixture in the form of briquettes.

The preparation of the ferro-chrome alloys of the kind specified by such a process presents certain difficulties. The high percentage of chromium required in the alloys necessitates a relatively large bulk or proportion of mixed chromite and reducing reagent to be added to the molten steel to produce an alloy containing a sufficiency of chromium; the reagents employed must be cheap for the process to be successful economically; the added reagents should be in a form in which they may be added readily at the requisite time; and they should be of such a character that there is not introduced into the finished alloy elements such as carbon which would spoil or which would present special difficulties in securing their elimination from the finished product.

In the process according to one example of the invention I proceed as follows:—Finely ground and prepared chromite and fluxes such as lime and fluorspar are mixed with the calculated or requisite amount of low carbon or substantially carbon free silicon, ferro-silicon, calcium silicide or other cheap silicon-alloy reducing reagent necessary to reduce the ore to metal. The amount of this mixture necessary to produce a ferro-chrome alloy of the required chromium content is then added to a prepared molten mild or low-carbon steel bath. The heat of the molten steel causes a reaction between the chromite and the admixed reducing reagent, liberating metallic chromium and iron which dissolves or alloys with the steel and forms the ferro-chrome-alloy. The alloy thus prepared is low in carbon, and it is freed from any excess of silicon by oxidation, such as by a blowing operation in a converter. As is well-known silicon readily oxidizes by such treatment, and it can be eliminated to the extent required before oxidation of the chromium occurs.

In addition to the reducing agents specified a

certain proportion of aluminium, ferro-calcium, calcium-silicon-aluminium alloy, or other such more energetic deoxidizer may be used to form part of the reducing agent for the chromite. Such addition or additions make the reaction more energetic when the chromite-reducing mixture is added to the molten steel; by this means the danger of premature cooling of the molten steel is avoided or minimized, and a more fluid slag obtained, an advantage in securing the removal of the slag during the alloying operation.

If the amounts of material required in this process are considered, when using calcium silicide, as the reducing reagent, there would be required approximately 1,000 lbs. of chromite calcium silicide reaction mixture to be added to one ton of molten steel to procure a ferro-chrome alloy containing approximately 12% of chromium. Using 90 to 95% ferro-silicon and/or a proportion of aluminium the amount of the reaction mixture would be less. In any case the weight and volume of the material to be added to the molten material is considerable. To facilitate the introduction of this material I propose to form the powdered chromite-reducing mixture into briquettes which incorporated with a little neutral silicate of soda and moulded under pressure, will have less volume than when the loose powdered mixture is employed. Further, by making the briquettes of a standard weight, these units enable the alloying operation to be more readily effected.

I may cause the reaction and alloying operation to be effected in a Bessemer converter. For a known weight of mild or low carbon molten steel contained in a converter, which may have been freshly prepared by blowing molten pig iron, a number of chromite-reducing mixture briquettes or units are added forming part of the total charge to be added to obtain an alloy of the desired chromium content. The heat of the molten metal raises the temperature of the reaction mixture, causing the chromite to be reduced, heat being evolved. The chromium liberated dissolves in the molten steel, and the lime and silica formed as by-products of the reaction form a fluid slag. More briquettes are added when the first additions have dissolved or disappeared, fresh briquettes being added as found convenient. The slag which forms and collects on the surface may be removed from time to time either by tipping the converter, or by providing an adjustable opening in the side through which the slag may be run off. The converter may be formed or provided with flexible air blast connections whereby when the converter is tipped the blast may play upon the surface of the slag or metal to help in the removal of the slag out of the converter throat. Suitable fluxes may be added to render the slag more fluid to facilitate its removal. If desired, the alloying operation may be effected in two or more converters, the alloy steel being run off from one converter into another to separate it from the slag, and the alloying operation continued or finished in the fresh converter.

The reaction between the chromite and calcium silicide or other like reduction reagents evolves heat and this should be sufficient to maintain the converter charge in a fluid and molten state. If this heat is too vigorous, it may be reduced by blowing through or on to the charge a steam containing blast.

If it is inclined to be cooled during the manipulation of the converter to effect the discharge of slag, air or air enriched with oxygen may be blown through the converter charge from time to time. The occasional use of the blast is desirable also in order that the steel and alloy metal may be thoroughly mixed.

The use of a silicon alloy as the reducing reagent for the chromite is also especially suitable as providing a medium whereby the heat of the molten metal may be increased or maintained at any time by the use of the blast through the charge. It also oxidizes so readily by this means that there is but little danger of loss of chromium from the steel by oxidation. Extra silicon material may be added for this purpose, if required.

While I have described the operation as taking place in a converter, it will be readily understood that an electric furnace may be used. Preferably an induction furnace would be used in this case in order to avoid the introduction of carbon into the molten alloy steel. The furnace should also be a tipping furnace so that the excess of slag formed may be removed from time to time, as desired.

By the process and means described there is thus produced a ferro-chrome alloy having a chromium content such as is required for a rustless iron or stainless steel alloy. As the materials employed are free or substantially free from carbon the alloy should also be free or substantially free from carbon. The silicon content in excess of that required in the alloy is now removed by subjecting the alloy to a further blowing operation either in the same or in a fresh converter, any sulphur or phosphorus being also removed in a manner well known in converter practice.

The blowing operation may also be effected by the means described in my co-pending British Patent application No. 4,809 filed 18th February 1922 which also includes the injection of a flux and solid oxidizing ingredients.

Instead of using a blowing operation for refining the iron-chromium alloy to remove by oxidation any excess of silicon above that required in the final alloy I may employ solid refining ingredients in the form of reducible oxides and/or oxygen containing compounds, as described in prior British Patent applications Nos. 7,831 of the 17th March, 9,422 of the 1st April and 18,009 filed 30th June all of 1922; by the employment of molten or fused alkali as described in British Patent application No. 7,832 of the 17th March 1922; by the employment of appropriate carbonates as described in British Patent application No. 7,833 of the 17th March 1922. Further, in my prior British Patent application No. 9,421 of the 1st of April 1922, I have referred to the refining of such chromium steels by the use of the above solid ingredients separately or in combination, followed by a subsequent and final blowing operation employing refining gases or gaseous mixtures of a refining character; or this blowing operation may precede the refining by the use of oxides and/or reducible compounds as stated in my British Patent application No. 18,009 dated the 30th June 1922.

The following specific refining agents taken from those British applications may thus be utilized in the refining operations set forth herein. Any readily reducible metallic oxide or oxides, the metal or metals of which form a constituent of the desired refined ferro-alloy may be employed. For example, oxides of iron such as hematite, and chromite. Such reducible metallic oxides may be used with alkaline earth and alkali metal compounds, or the latter may be

used by themselves, among which we may mention alkaline earth oxides, and/or alkali metal carbonates, and/or alkali. Sodium nitrate or barium peroxide may be employed. Desirable mixtures of such ingredients, such as chromite and a carbonate may be employed. Manganese oxide and peroxides, such as barium peroxide, either alone or in admixture with other reducible oxides may be utilized. Bicarbonates of the alkali metals may be utilized. Pure carbonates such as those of calcium, sodium and/or potassium may be employed with the oxides, and also a proportion of sodium and potassium hydroxide if desired. Other types of solid compounds that may be employed in the purification include titaniferous iron ore, sulphates, such as of iron, chromium, manganese, sodium, potassium, calcium, aluminum, magnesium etc., the bisulphates, such as of potassium and sodium; the cromates of calcium and magnesium; and hydrates as of lime and magnesia. These several purifying agents specified above may be employed desirably in combination with a fluoride, such as fluorspar, or other fluorine containing compounds, such as cryolite, the fluorides of sodium and aluminum, the fluo-silicates of calcium and the like. Further illustrating the types of oxides which yield metals in the final alloy, reference may be made in addition to manganese referred to above, nickel, tungsten and similar oxides, sodium ditungstate, etc.

Where a refining blast is used, the refining agents may be injected with such blast, employing principally or entirely steam, and/or carbon dioxide or another oxidizing blast. Preferably the nitrogen content of the blast is kept low or entirely eliminated. Hydrogen or oxygen may be used admixed with the steam and/or carbon dioxide blast.

The disadvantage of employing a reducible ore or compound such as chromite as the sole means of alloying a sufficiency of metallic chromium with the steel to form a chromium-containing rustless or nonstainable steel is that the quantity of slag formed is unduly high, rendering the process somewhat troublesome in operation and with a danger that billets formed from the alloy steel may have undesirable slag inclusions. To remove or minimize these disadvantages I find it desirable to add a proportion of metallic chromium or a chromium alloy to the molten steel. This chromium alloy may be in the form of ferro-chrome, or an iron-chromium silicon alloy, or an iron chromium nickel alloy containing a little or an excess of silicon. This metal or alloy component may be employed as part of the briquettes or the powdered reaction mixture to be added to or injected into the molten steel, or it may be added separately and it may be added at any stage of the alloying operation, as may be considered best or found most practicable to facilitate the production of the desired alloy.

When the chromium metal or alloy employed is used as part of the briquettes it is of service to weight them, and by thus increasing their specific gravity it causes them to sink more readily under the surface of the molten steel. Further, the total quantity of material to be added to the molten steel to produce the alloy of the desired composition is reduced because there is a less quantity of reducible oxide or compound of chromium necessary. When a chromium silicon alloy is employed the silicon in this alloy may be made use of as a reducing agent for an equivalent (or less) of the reducible oxide and/or compound employed with the reaction mixture.

Thus, a briquette may be composed of chromite, ferro-silicon, and iron chromium silicon alloy, the chromite being in a quantity to be reduced substantially by the silicon in the ferro-silicon and iron-chromium-silicon-alloy. Or if the chromium steel is desired to contain a final proportion of silicon, the ferro-silicon and chromite may be in equivalent proportions, the silicon in the ferro-chrome or nickel-iron-chrome alloy then forming a component of the final steel alloy, as will be understood. Or a briquette composed mainly or wholly of a ferro-chrome with a high silicon content and chromite (or green oxide of chromium) may be employed.

A similar procedure may be adopted where the thermo reduction or reaction mixture is to be employed as a powder and introduced into the molten steel by injecting the material into a container like a converter; or both methods of means may be adopted.

Some stainless or weather resisting steels or irons advantageously contain also a substantial percentage of nickel. All or part of the nickel required may be alloyed with the steel by employing it as a silicon or silicon-chromium-iron alloy in a manner similar to that previously described.

The advantage of employing chromium as an alloy containing silicon is that it may be readily and cheaply prepared with a low carbon content by reduction, in a preliminary operation, of, for example, chromite with a low carbon silicon containing reducing agent. By the use therefore, of such an alloy or alloys there need be little danger of introducing carbon in excess into the alloy steel. It may be desirable, however, to employ a more easily reducible oxide than chromite for reacting with the contained silicon in the chromium alloy when the reaction mixture is added to the molten steel. For this reason, desirably, the chromium-silicon-alloy is compounded or used with oxide of iron and/or green oxide of chromium, or sodium or calcium chromate, and so on, instead of with the more refractory material, chromite, or the silicon in the chromium alloy may be made to react with the oxide of nickel.

When a proportion of nickel is to be added to alloy with the molten steel to form part of the final alloy, the reaction mixture may be added to the molten steel in containers made of nickel, or the metallic nickel may be used as shot and compounded as part of the briquettes. These and similar means of employing the chromium alloy and/or chromium silicon-alloy and nickel and/or nickel silicon alloy for weighting the compounded briquettes or powder to be added to the molten steel may be employed, as will be understood. Thus, chrome steel or chrome iron or cast-ferro-chrome containers may be used.

The blowing operation, employing steam and/or carbon dioxide, with or without hydrogen, or air, may be used either before or after the use of the solid ingredients previously specified, as well as by employing such gases for injecting the said solid ingredients. Thus, for example, if a very low carbon steel is desired, I may form first a steel alloy containing chromium and excess of silicon by suitably proportioning the reaction mixture to be added to the molten steel. By this means the carbon present in the alloy tends to be precipitated or displaced by the excess of silicon from combination with chromium as the

carbide, and the molten alloy may then be blown with steam and/or carbon dioxide or treated with a decomposable carbonate or an alkali to reduce or eliminate the carbon content. Finally in such refining operations, the silicon in the alloy is eliminated or reduced by means of the solid ingredients previously referred to.

The refined alloy steel thus produced is finished by the addition of suitable deoxidizing material etc., as may be required.

I claim:

1. The process of making alloy steel, comprising forming a molten bath of steel in which is incorporated a reducing agent and an unreduced compound of the alloying metal, maintaining such bath in a heated condition to permit a reaction to take place between the reducing agent and the unreduced compound of the alloying metal whereby the alloying metal is reduced directly to metallic form in the bath, and finally increasing the temperature to substantially eliminate any reducing agents from the finished steel, substantially as described.

2. The process of making chrome steel, comprising forming a bath of steel in which is incorporated a non-carbonaceous reducing agent and an unreduced compound of chromium, maintaining such bath in a heated condition to permit a reaction to take place between the reducing agent and the unreduced compound of chromium whereby the chromium is reduced directly to metallic form in the bath, and finally increasing the temperature in the oxidation of excessive reducing material.

3. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon, phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

4. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow under application of external heat.

5. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy of iron and chromium having a chromium content of substantially between 9 and 16% and uncontaminated with carbon phosporus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

6. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

7. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon ferro-silicon, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

8. The manufacture of unstainable metal which comprises reducing chromite within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

9. The manufacture of unstainable metal which comprises reducing chromite within a molten ferrous bath of low-carbon content, by means of a low-carbon ferro-silicon, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

10. The manufacture of unstainable metal which comprises diluting with molten recently blown Bessemer metal, the iron-chromium product of reducing substantially non-carbonaceous compound of iron and chromium with a low-carbon silicon reducer so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

11. The manufacture of unstainable metal which comprises diluting with molten recently blown Bessemer metal from which the Bessemer-

izing slag has been removed, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorus and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

12. The manufacture of unstainable metal which comprises diluting with molten steel of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

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