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METALLURGY

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This invention relates to metallurgy and has for an object the provision of an improved method or process for producing ferro-alloy products. More particularly, the invention contemplates the provision of an improved method or process for producing ferro-alloy products of uniform compositions. A particular object of the invention is to provide an improved method or process for producing ferro-alloy products comprising iron and chromium such, for example, as low-carbon ferrochromium. A further object of the invention is to produce improved ferro-alloy products comprising low-carbon ferrochromium.

The expression "low-carbon ferrochromium," as herein employed is intended to define crude alloys consisting essentially of iron and chromium and used chiefly to incorporate chromium in iron or steel, alloys of the types and compositions, for example, of those produced according to heretofore customary procedures by reducing chromite ore directly with carbon to produce high-carbon ferrochromium, incorporating silicon in the high-carbon ferrochromium to remove carbon, and treating the resulting product with oxidizing material to remove excess silicon with the production of low-carbon ferrochromium containing chromium and iron in substantially the same ratio as in the high-carbon ferrochromium produced initially.

According to some heretofore customary practices, ferro-alloys are produced by reducing compounds of iron and alloying elements such, for example, as chromium, silicon, manganese, vanadium, tungsten, titanium and molybdenum at elevated temperatures in suitable furnaces with the production of molten baths of the ferro-alloys, the relative proportions of iron and alloying elements in the final alloy products being determined by the relative proportions of iron and the alloying elements present in the furnace charges. The amount of ferro-alloy, or the size of the molten bath of ferro-alloy, produced in any particular operation is determined by the capacity of the apparatus employed. Ferro-alloys are produced, usually, in electric furnaces of the submerged arc type which operate continuously to produce ferro-alloys but from which the ferro-alloys are tapped intermittently at spaced time intervals. The amount of ferro-alloy tapped from a furnace each time may be small or large, depending upon the furnace construction and capacity and its operating characteristics.

Ferro-alloys are employed in industry in the form of solid pieces which are relatively low in weight as compared with the weight of the molten ferro-alloy metal baths produced in the furnace operations. According to some heretofore customary practices, solid pieces of ferro-alloy of sizes useful in industry are produced by pouring the bulky or massive molten alloy product of a furnace into a chill in the form of a shallow metal pan, permitting the molten metal to solidify, and breaking the solidified massive metal products into smaller pieces, as, for example, pieces measuring about two to six inches in greatest diameter, by means of hammers.

As produced in a properly operated furnace, the molten ferro-alloy product is of uniform composition throughout. As cooling and gradual solidification take place in the chill, however, the composition of the metal product becomes non-uniform owing to the formation of compounds of the iron with the one or more alloying elements present which have different freezing temperatures. Thus, for example, iron and chromium are capable of forming many compounds containing iron and chromium in different proportions and which freeze at different temperatures and segregate as solidification of the molten product takes place slowly. When carbon is employed as the reducing agent, as in the case of ferrochromium production, some carbon is present in the molten furnace product and further influences segregation and the production of non-uniform products by forming with iron and the one or more alloying elements present compounds having different freezing temperatures. The proportions of iron and alloying element in various portions of a solidified furnace product may vary as much as ten percent or even more. Thus, for example, in a solidified mass of high-carbon ferrochromium formed in a shallow chill, the material in the central portion may contain about seventy percent of chromium, the material in the outer portions may contain as little as sixty percent of chromium and the material in the intermediate portions may contain chromium in various amounts ranging from sixty to seventy percent.

Ferro-alloys are used largely for metallurgical purposes as addition agents for incorporating alloying elements in molten iron and steel to produce iron and steel products of rather rigid specifications with respect to contents of alloy elements. The non-uniform character of the products of ferro-alloy furnaces produced in accordance with heretofore customary practices has complicated the problem of adding ferro-alloys to iron and steel in proper amounts to meet rigid specifications with respect to contents of alloy elements, and the production of iron and steel products of proper compositions involves considerable difficulty. The problem of adding ferro-alloys to iron and steel in proper amounts to meet rigid specifications is complicated not only by the fact that various portions of any particular solidified product of a furnace may be of different compositions, but also, by the fact that products formed in and tapped from the same furnace at different times differ in compositions

from one another as well as within themselves, since a shipment of ferro-alloy from a ferro-alloy producer to a steel plant for use may be made up of products produced in and tapped from the furnace at different times. Such shipments may be made up also of non-uniform products of several different furnaces. A single shipment of ferro-alloy may be employed by the steelmaker as source of ferro-alloy for making numerous heats of alloy iron or steel over a substantial period of time. Various portions of a particular shipment may have widely different chemical compositions, and, consequently, the results obtained in the use of a portion of a shipment of ferro-alloy for producing one heat of iron or steel can not be relied upon when using another portion of the same shipment to produce other heats of iron or steel.

The non-uniform character of commercial grades of ferro-alloys available to producers of alloy iron and steel products is illustrated by the following table appearing on page 20 of volume I of Alloys of Iron and Chromium (McGraw Hill Book Company, Inc., New York, 1937) and setting forth typical analyses of various grades of ferrochromium:

Element	Composition, per cent, for grade containing maximum carbon percentage of—				
	0.06	0.50	2.00	4.50	Over 7.00
Chromium	68–72	68–72	68–72	67–71	66–70
Carbon	0.05–0.06	0.2–0.5	1.0–2.0	4.0–4.5	7.0–9.0
Silicon	0.2–0.8	0.2–0.8	0.5–1.0	1.0–3.0	1.0–3.0
Sulphur	0.01	0.01	0.02–0.05	0.05–0.10	0.05–0.10
Phosphorus	0.01–0.03	0.01–0.03	0.01–0.03	0.01–0.03	0.01–0.03

Ferro-alloys such as ferrochromium products may be sold to the alloy iron or steel producer under specifications covering the relatively wide ranges of percentages of all components or constituents illustrated by the above table. Under the circumstances it is difficult or impossible for an alloy iron or steel producer to predict accurately the final composition of a product formed by adding to a molten metal bath a quantity of the ferro-alloy.

The present invention contemplates the elimination of difficulties encountered heretofore in the incorporation of chromium in iron and steel to meet rigid specifications with respect to chromium and carbon.

In accordance with the present invention, the massive product of the ferro-alloy furnace producing low-carbon ferrochromium is so treated as to form a relatively finely divided product of substantially uniform chemical composition throughout. In a preferred method or process of the invention, the molten product of a ferro-alloy furnace is chilled rapidly to a temperature below the freezing temperature of the lowest freezing-point compound which might be formed by the components or constituents of the ferro-alloy. A final substantially uniform product formed in accordance with the invention may comprise low-carbon ferrochromium obtained by tapping a single furnace one or more times or by tapping two or more similarly operated furnaces one or more times each.

Rapid chilling and granulating, or finely dividing, may be accomplished in any suitable manner, as, for example, by directing a jet of relatively cold gas (such as steam or air) under pressure or liquid (such as water) against a stream of the molten ferrochromium or by pouring the molten ferrochromium into a large volume of water. Rapid chilling of a stream of molten ferrochromium results in the production of a relatively finely divided or granulated solid product consisting of pieces or particles all of which are of substantially the same chemical composition. The sizes of the particles produced will be determined largely by the rate of chilling or by the relative proportions and temperatures of the molten ferrochromium and chilling agent.

For effective chilling and granulation of the ferrochromium, I may direct one or more jets of cold water against a stream of the ferrochromium as it pours from the furnace. Preferably, I pour the molten ferrochromium in such manner that the metal passes downwardly through two or more vertically spaced streams of water flowing transversely of the direction of flow or fall of the metal. The streams of water preferably are formed by flowing the water under about forty pounds per square inch pressure, more or less, through nozzles having substantially rectangular outlet orifices of such dimensions as to form flat wide streams, that is, streams having greater horizontal than vertical dimensions. The widths and depths of the streams of water will be determined in each case by the size of the stream of metal and its rate of flow. Granulation may be effected substantially entirely by chilling, or the pressure or force of the granulating fluid employed may be such that granulation is assisted also by mechanical disruption of the molten metal.

Products produced by granulation with water may be deposited directly on perforated conveyors to permit de-watering. The conveyors may carry the products to drying apparatus for final elimination of the water.

The granulating feature of the invention may be employed advantageously in conjunction with bonding operations to form agglomerates larger than the particles produced by granulation and in conjunction with grinding operations to form particles smaller than those produced by granulation. Grinding operations and granulating and grinding operations of the invention also may be employed advantageously in conjunction with bonding operations to form agglomerates larger than the particles produced by grinding.

When the ferrochromium is to be employed for incorporating chromium in steel or iron by placing the ferrochromium in the solid state on the surface of a slag covered molten bath of steel or iron, the particles of a uniform product formed in accordance with the invention may be too small to penetrate the slag satisfactorily. In order to avoid difficulties which might result in such cases, I may bond together sufficient numbers of particles to form masses of suitable sizes. The particles may be molded in any suitable shapes and sizes and bonded together by means of any suitable bonding agent under such conditions as to produce dry, or water-free, solid products. Sodium silicate, Portland cement, sodium carbonate or sodium nitrate or any combination of two or more of these substances may be employed satisfactorily for bonding the particles.

When the ferrochromium is to be employed in solid reaction mixtures, the granulated particles may be too large to permit sufficiently intimate contact with other components of the reaction mixtures. In such cases, I may subject the particles to a grinding treatment in a ball mill or other suitable apparatus to produce

smaller particles of suitable sizes. Granulation with a chilling agent such, for example, as water followed by grinding may be employed advantageously to facilitate the production of particles of very small sizes. Granulation with water is relatively inexpensive and grinding is relatively costly. The use of granulation with water in conjunction with grinding results in greater efficiency at a lower cost. Granulation in water followed by grinding also permits the production of very small particles of some chromium-bearing ferro-alloys which otherwise could not be ground to such small sizes at all, or, if at all, only with the greatest difficulty. Thus, for example, low-carbon ferrochromium containing substantially less than about five per cent of silicon can be ground in ball mills and similar apparatus to produce particles small enough to pass a 100-mesh screen only with the greatest difficulty when the pieces of ferrochromium subjected to the grinding treatment initially are of the sizes of those available heretofore. Such low-carbon ferrochromium products can be granulated by treatment with water to form particles ranging in size from about one-sixteenth inch and smaller to about one-quarter inch and most of which are smaller than one-quarter inch. Such particles may be ground to produce particles small enough to pass a 100-mesh screen with little or no difficulty.

Low-carbon ferrochromium products which may be employed more advantageously in the production of alloy steel and iron than products formed heretofore may be produced by chilling and granulating the molten ferrochromium. When a ferrochromium product to be produced, as, for example, for making up a single shipment to a steel plant, is to include ferrochromium tapped from a furnace at different times or ferrochromium produced in two or more similarly operated furnaces, the finely divided particles, whether produced by chilling and granulation or by chilling and granulation followed by grinding, should be mixed intimately. Satisfactory intimate mixing can be achieved with particles produced simply by chilling and granulating molten ferroalloy, but more effective intimate mixing can be achieved with the smaller particles which can be produced by grinding of particles produced by chilling and granulation.

In forming uniform ferrochromium products comprising ferrochromium tapped from the furnace at different times or produced in two or more similarly operated furnaces, I prefer to produce finely divided products consisting largely of particles small enough to pass a 10-mesh screen.

Uniform ferrochromium products formed in accordance with the invention may be sold to steel manufacturers and employed in the manufacture of steel and iron products in granular or finely divided form or in agglomerated form, but I prefer to prepare uniform ferrochromium products for use by steel and iron manufacturers in the form of agglomerates comprising relatively small particles of the ferrochromium products. Bonding of the particles of ferrochromium products aids in preventing segregation of particles of different compositions in any particular batch of material and insures delivery to the steel manufacturer of products of substantially uniform composition throughout and comprising units or agglomerates all of which are of substantially the same composition. The production of agglomerates aids producers of alloy iron and steel products by providing masses of ferrochromium products of suitable sizes for penetrating slag layers overlying molten iron and steel baths.

Agglomerates produced in accordance with the invention may consist essentially of finely divided low-carbon ferrochromium and bonding material which is substantially inert or non-reactive with respect to the ferrochromium or they may comprise finely divided ferrochromium and reactive material. Agglomerates consisting essentially of ferrochromium and substantially inert or non-reactive bonding material can be employed to perform the same functions as those for which pieces of solid low-carbon ferrochromium have been employed in accordance with heretofore customary practices. Agglomerates of the invention may constitute exothermic reaction mixtures of the types of those described in my United States Patents Nos. 2,176,688, 2,243,783, 2,243,784, and 2,243,786, and in my copending application Serial No. 303,363, filed November 8, 1939, in which the ferro-alloy is associated with one or more materials capable of reacting with one another or with a component of the ferro-alloy. The invention may be employed advantageously to produce exothermic reaction mixtures comprising a low-silicon silicide of an alloy metal such, for example, as low-silicon ferrochrome silicon (or high-silicon ferrochromium) containing not more than about five percent of silicon and oxidizing material, such as sodium nitrate, capable of reacting with the silicon of the ferrochrome silicon to generate heat for melting the iron and chromium. Such reaction mixtures require ferrochrome silicon in the form of small particles, preferably small enough to pass a 100-mesh screen, and, as hereinbefore pointed out, particles of such small size are difficult to produce by direct grinding but can be produced quite easily by water chilling and granulation followed by grinding.

I claim:

1. In the production of a ferro-alloy product suitable for use as an addition agent for incorporating an alloying element in molten iron or steel, the improvement which comprises finely dividing low-carbon ferrochromium by chilling and granulating from the molten state and forming a product comprising solid particles of low-carbon ferrochromium and of substantially uniform chemical composition.

2. In the production of a ferro-alloy product suitable for use as an addition agent for incorporating an alloying element in molten iron or steel, the improvement which comprises finely dividing low-carbon ferrochromium by chilling and granulating from the molten state with water and forming a product comprising solid particles of low-carbon ferrochromium and of substantially uniform chemical composition.

3. A product suitable for use as an addition agent for incorporating chromium in molten iron or steel comprising solid particles of low-carbon ferrochromium formed by chilling and granulating molten low-carbon ferrochromium.

4. A product suitable for use as an addition agent for incorporating chromium in molten iron or steel comprising solid particles of low-carbon ferro-chromium formed by chilling and granulating molten low-carbon ferrochromium with water.

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