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PROCESS FOR PRODUCING A COLUMBIUM ADDITION AGENT

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5 Claims. (Cl. 75—206)

This application is a division of U.S. Ser. No. 81,683, filed on January 10, 1961, now U.S. Patent 3,143,788.

The present invention relates to a novel process for producing columbium addition agents directly from oxidic columbium starting materials and high-carbon ferrochromium.

In the manufacture of stabilized stainless steels it is common practice to add to the steel bath a strong carbide-forming element such as columbium in an amount equivalent to about eight to ten times the carbon content. The columbium effectively combines with the carbon and prevents carbide precipitation during operations requiring heating of the steel, such as welding, thus avoiding the known deleterious effects of carbon on the corrosion resistance properties of the steel.

Ferrocolumbium has been used for this application but because of its greater density the alloy generally sinks to the bottom of the steel bath and is slow to diffuse through the melt.

Ferrocolumbium is prepared by a rather complex and expensive process usually comprising fusion with iron or iron ore and a reductant to remove associated tin, followed by carbiding of the resulting slag to separate the columbium from the other constituents thereof and finally smelting the carbide with iron ore to produce ferrocolumbium.

It is an object of the present invention to provide a novel columbium-containing low-carbon ferrochromium addition alloy which is less dense and more readily soluble in molten metallic baths.

It is another object to provide a process for producing columbium-containing, low-carbon ferrochromium directly from oxidic columbium starting materials and high-carbon ferrochromium at low temperatures.

It is a further object to provide a process for producing substantially tin-free, columbium-containing, low carbon ferrochromium directly from tin-containing oxidic columbium starting materials and high-carbon ferrochromium at low temperatures.

The product satisfying the above mentioned objects comprises sintered, columbium-containing, low carbon ferrochromium alloy addition agent having an apparent density ranging from 6.5 to 7.5 grams per cubic centimeter and being characterized by its ability to float on the molten melts to which they are added, and comprising 5 to 20 weight percent columbium, 45 to 65 weight percent chromium, less than 2.0 percent silicon, less than 0.5 weight percent carbon, less than 0.10 weight percent tin, less than 0.03 weight percent sulfur and the remainder iron and incidental impurities.

The process achieving the above-mentioned objects and providing the above-mentioned novel addition alloy comprises admixing a particulate, high-carbon ferrochromium, a particulate, oxidic columbium starting material, and a suitable binder, compacting the admixture to form a coherent body, heating the body in vacuo at a pressure less than about 3.0 mm. of Hg and to a temperature below about 1500° C. and reacting the carbon in the high-carbon ferrochromium with the oxygen in the oxidic columbium containing starting materials to cause reduction of columbium and evolution of carbon oxide,

continuing heating until the evolution of carbon oxides substantially subsides and removing the resultant sintered, low-carbon, columbium-containing, ferrochromium.

It has been found, surprisingly and contrary to expectations, that, under the conditions specified in the process of the invention, columbium oxide compounds are reduced to the metallic state by the carbon contained in high-carbon ferrochromium. The reason for this unexpected result is not known, but it is thought that interdiffusion of the ferrochromium and the columbium favorably alters the equilibrium of the reduction reaction. This is supported, in part, by data secured from X-ray diffraction examinations which disclosed the presence of the compound Fe_2Cb in the final product.

As disclosed in the U.S. Patent 3,091,624, issued on May 28, 1963, it is known that columbium metal may be produced by heating an intimate mixture of pure oxide and carbon. It has been found necessary to heat such mixtures to a temperature in the range of 2000° C. to 2200° C. in order to avoid the formation of columbium carbide as the final product rather than the desired pure metal. Columbium carbide has no use in stainless steelmaking. Since columbium is utilized in stainless steel making to counteract carbon, there is no advantage to adding columbium carbide to stainless steel.

High-carbon ferrochromium commonly contains 4.5 to about 7.0 weight percent carbon. Low carbon ferrochromium commonly contains 0.025 to about 2.0 weight percent carbon. Throughout the remaining disclosure and appended claims, the above-identified high-carbon and low-carbon ferrochromium alloys will be utilized to indicate the reactants and products.

Columbium oxide starting materials are obtained from a variety of sources and the tramp oxides present in the starting material vary accordingly. Ta_2O_5, Fe_xO_y, Mn_xO_y, SiO_2 and tin oxides are commonly present in oxidic starting materials. Tin oxide is a common and persistent contaminant of columbium oxide starting material due to the close association of the oxides of tin and columbium in mother ores. Since tin is an undesirable element in steel, it must be eliminated from alloy addition agents used in steel-finishing. Virtually all oxidic columbium from known sources may be utilized as a starting material in the present process including tin-containing oxidic columbium starting materials.

Any suitable organic or inorganic binder may be employed. Such binders are known in the art and include chromic acid, molasses, starches, chromium or iron formate solutions and the like.

The particle size of the material utilized in the starting admixture will affect the rate of the reaction. It has been found that the particle size of the oxidic columbium starting material can be in the range of from about 100XD to about 325XD (Tyler Mesh) and preferably about 100XD (Tyler Mesh). Particle size of high-carbon ferrochromium can be in the range of from about 200XD to about 400XD (Tyler Mesh) and preferably about 300XD (Tyler Mesh).

The reaction in the present process is essentially a solid state reaction carried out in vacuo. The pressure during the reaction is maintained below about 3.0 mm. of Hg.

Heating rates are important. It is essential that the rate of temperature rise during the reaction does not cause the temperature of the pressed forms to exceed the eutectic melting point of the combination of compounds in the compacts. By the same token it is desired to cause sintering of the pressed forms. Incipient melting of the particle in the compact will seal the interstices of the compact and prevent outward flow of the carbon oxides resulting from the decarburizing reaction. As a result the reaction will be stopped. In many instances it

has been found that sintering can be caused without incipient melting of the particle. This is due to mass diffusion of the metals between particles. In the present process the temperature is caused to increase at a rate whereby sintering does take place yet mass melting of the compact is not produced. Sintering will take place at temperatures will below the eutectic melting point of the product produced by the present process.

The maximum temperature utilized in the present process is 1500° C. Temperatures in excess of 1500° C. cause melting of the compacts. The practical lower temperature limit is about 1200° C. Temperatures lower than about 1175° C. cause slow reaction rates and poor heat penetration.

As previously stated, the present process is essentially a solid state reaction. During the reaction, carbon from the high-carbon ferrochromium reacts with oxygen from the oxidic columbium starting material to cause evolution of carbon oxides. The temperature of the reactant mass is maintained until the evolution of carbon oxides substantially subsides. At this point the reaction is substantially completed and the resultant product is cooled and removed from the furnace.

The molar ratio of oxygen in the oxidic columbium starting material to carbon in the high-carbon ferrochromium of the starting admixture is maintained substantially in the range from about 1.0 to about 1.2. The preferred molar ratio is about 1.10.

The product of the present invention is characterized, in addition to the above-noted composition, by its density which ranges from 6.5 to 7.5 grams per cubic centimeter.

Compaction of the starting admixture is accomplished in accordance with well known methods.

As stated in the objects, the present process can be advantageously utilized to produce columbium-containing low-carbon ferrochromium with a low tin analysis from oxidic columbium starting materials containing substantial amounts of tin. This is accomplished by adding a sulfur-bearing material to the starting admixture in sufficient amounts to react with the tin in the columbium starting material to form a tin sulfide. Tin sulfide is volatile under the operating conditions of the present process and is eliminated with the evolved carbon oxides.

It has also been observed that the addition of as little as 20 to 50 percent of the sulfur required to react stoichiometrically with the tin in the starting material results in satisfactory removal of tin during the process. This may be due to volatilization of part of the tin as an oxide. At any rate, the upper limit of sulfur utilized in the present process is about the stoichiometric amount required to react with all the tin in the starting materials.

The particle size of the sulfur bearing material in the starting admixture can range from 100 Mesh by Down to 325 Mesh by Down (Tyler Mesh) and preferably is 100 Mesh by Down (Tyler Mesh).

The sulfur-bearing material utilized in the present process preferably has lower vapor pressure than tin sulfide for a given temperature. An example of a sulfur-bearing material which may be utilized in the present process is iron sulfide. It should be noted that any sulfur in the ferrochrome may assist in tin removal. Elemental sulfur may possibly be utilized although it may volatize under the process conditions before reacting with the tin in the starting materials. This innovation permits an artisan to utilize columbium oxide starting materials containing tin to produce substantially tin-free, columbium-containing, ferrochromium, thus eliminating steps normally required to remove tin from columbium oxide to be utilized in the production of alloy addition agents.

The following examples will serve to illustrate the present process.

In all the examples the ferrochromium, the columbium source materials, and the sulfur-bearing materials were nominally 300 (Tyler Mesh) by Down, 100 (Tyler Mesh) by Down and 100 (Tyler Mesh) by Down respectively.

The starch binder utilized in all examples was nominally 100 (Tyler Mesh) by Down in particle size. All the starting admixtures were pressed into coherent forms by standard techniques and a vacuum resistance furnace was utilized to heat the mixture.

Example I

An admixture was prepared by intimately blending: 11.8 pounds of oxidic columbium starting material containing 66.05 weight percent Cb_2O_5, 6.5 weight percent Ta_2O_5, 18.94 weight percent FeO, 2.18 weight percent MnO and 2.30 weight percent SnO_2; 40.0 pounds of high-carbon ferrochromium containing 66.68 weight percent Cr, 24.08 weight percent Fe, 4.95 weight percent C and 0.061 weight percent sulfur; with 0.8 pound of starch binder and 3.2 pounds of water. The admixture was pressed into bricks 5 inches by 5 inches by 10 inches and the bricks were dried at 400° F. for about 12 hours. The bricks were charged into a vacuum furnace, the furnace was sealed and the pressure was reduced to 150 microns. The furnace temperature was raised to about 1000° C. over a period of six hours, held at 1000° C. for 4 hours and then raised to 1385° C. over a 5 hour period. A temperature of 1385° C. was maintained for 72 hours after which the furnace was allowed to cool at a rate dependent solely on the natural heat loss. The product obtained analyzed 55.0 weight percent chromium, 12.0 weight percent columbium, 0.49 weight percent carbon, 1.97 weight per silicon, 0.18 weight percent tin, 3.2 weight percent O_2 and 0.018 weight percent sulfur, 0.01 weight percent CaO+MgO, 0.82 weight percent Al_2O_3 and the remainder iron.

Example II

Following the procedure of Example I two mixtures were prepared analyzing as follows:

Mixture I.—11.7 pounds of oxidic columbium starting material containing 95.5 weight percent Cb_2O_5, 1.3 weight percent Ta_2O_5 and 0.034 weight percent FeO; 40 pounds of high-carbon ferrochromium having the same analysis as that utilized in Example I; 1 pound of starch binder and 3.2 pounds of water. The molar ratio of oxygen to carbon was 1.2.

Mixture II.—13.7 pounds of oxidic columbium starting material containing 51.24 weight percent Cb_2O_5, 0.5 weight percent Ta_2O_5, 19.98 percent FeO, 8.6 weight percent SiO_2 and 0.02 weight percent SnO_2; 40 pounds of high-carbon ferrochromium having the same analysis as Example I; 1 pound of starch binder and 3.2 pounds of water. The molar ratio of oxygen to carbon was 1.2.

The above Mixtures I and II were pressed into bricks of the size shown in Example I and dried and furnaced in the manner shown in Example I except a part of the bricks resulting from each Mixture I and II above were treated for 2 hours at 1360° C. followed by 20 hours at 1450° C. The products resulting from Mixture I above analyzed 56.33 weight percent Cr, 17.4 weight percent Cb, 0.01 weight percent C and 1.6 weight percent O_2 and the reaminder iron and incidental impurities.

The products resulting from Mixture II analyzed 57.10 weight percent Cr, 9.0 weight percent Cb, 0.32 weight percent C, 2.3 weight percent O_2 and the remainder iron and incidental impurities.

The remaining bricks resulting from each of the above Mixtures I and II were treated at a temperature of 1360° C. for a period of 40 hours. The bricks resulting from Mixture I contained 0.06 weight percent C and the bricks resulting from Mixture II contained 0.10 weight percent carbon.

Example III

Three mixtures were prepared to illustrate the effect of the molar ratio of oxygen to carbon on carbon removal and also elimination of tin by sulfur addition.

The columbium source material contained the following:

Compound:	Weight, percent
Cb_2O_5	66.51
Ta_2O_5	6.25
FeO	18.43
SiO_2	2.06
SnO_2	2.96

The high-carbon ferrochromium contained the following:

Element:	Weight, percent
Cr	67.02
Fe	24.20
C	4.90
S	0.06

Iron sulfide having 36 weight percent sulfur was utilized as the sulfur-bearing material.

The proportions in pounds in each mixture were as follows:

Material	Mixture I	Mixture II	Mixture III
Cb source	60	10.9	11.4
High-carbon ferrochromium	200	40.0	40.0
Starch binder	5	1.0	1.0
FeS	None	0.14	0.14
Water	16.0	3.2	3.6
O_2/C molar ratio	1.1	1.0	1.05

The mixtures were pressed each into pillow-shaped pellets approximately 2 inches by 2 inches by 1.5 inches. The same heating procedure was employed as shown in Example I. A temperature of 1360° C. was maintained for 36 hours in treating the pellets from each mixture. The products resulting from each mixture contained the following:

Mixture	Fe	Cr	Cb	C	S	Sn
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
I	Bal	56.71	11.50	0.02	0.005	0.21
II	Bal	57.77	11.06	0.24	0.029	0.08
III	Bal	57.28	11.47	0.08	0.023	0.05

An 11 kilogram heat of A.I.S.I. 430 steel was prepared and the pellets resulting from Mixture III of Example III were charged in amounts sufficient to add 0.5 weight percent columbium to the melt. The addition was made at a bath temperature of 1600° C. The pellets floated on the surface of the melt and dissolved completely in 17.0 seconds.

Further data relating to the melting point and solubility of the alloys of the present invention in contrast to standard addition alloys are presented in the following Tables I–III.

TABLE I.—SOLUTION DATA FOR COLUMBIUM-BEARING ALLOY ADDITIONS MADE TO TYPE 430 STAINLESS STEEL AT 1600° C.

Alloy	Composition of Alloy	Percent Cb Added	Percent Cb in Steel	Percent Recovery	Solution Time, sec.
Present Alloy	Cr, 55.62 Cb, 11.7 C, 0.5 S, 0.008 Sn, 0.02	0.50	0.47	94	28
Present Alloy	Cr, 57 Cb, 12.9 C, 0.06	0.55	0.34	62	24
Std. FeCb	Cb, 58.21 Ta, 5.16 Si, 2.78 C, 0.07	0.50	0.42	84	20
Std. FeTaCb	Cb, 45.67 Ta, 15.91 Si, 6.15 C, 0.20	0.50	0.39	88	60

TABLE II.—MELTING RANGE DATA

Alloy	Composition	Temperature, ° C.	
		Solidus	Liquidus
Present Alloy	Cr, 56.66 Cb, 13.80 Si, 1.32 C, 0.01	1545–1570	1580–1585
Std. FeCb	Cb, 58.21 Ta, 5.16 Si, 2.78 C, 0.07	1680–1685	1720–1730
Std. FeTaCb	Cb, 45.67 Ta, 15.91 Si, 6.15 C, 0.20	1700–1715	1780–1785

TABLE III.—APPARENT DENSITY

Present Alloy	6.9–7.2 g./cm.^{3}	0.25/ft.^{3}.
Std. FeCb	8.4	0.30/ft.^{3}.
Std. FeTaCb	8.2–8.3	0.30/ft.^{3}.
Type 430 Steel at 1530° C. (Approx.)	6.9	

It should be noted that all the above alloys of the present invention floated on molten type 430 steel at a temperature of about 1530° C.

The foregoing discussion and the examples are illustrative. Modifications in the process without a departure from the spirit and scope of this invention will readily present themselves to the skilled artisan.

We claim:

1. A process for producing a sintered, columbium-containing, low-carbon ferrochromium addition agent which comprises admixing a particulate high-carbon ferrochromium, a particulate oxidic columbium material, and a binder; compacting the resulting admixture so as to form a coherent body, heating the coherent body under a pressure below about 3 mm. of Hg to a temperature below about 1500° C. but sufficiently high to react the carbon present in the ferrochromium with the oxygen present in the oxidic columbium materials; maintaining the coherent body at such temperature and pressure until the evolution of carbon oxides substantially subsides; and thereafter recovering the sintered, columbium-containing, low-carbon ferrochromium addition agent.

2. A process for producing a sintered columbium-containing, low-carbon ferrochromium addition agent comprising admixing particulate high-carbon ferrochromium and particulate oxidic columbium starting material and a suitable binder, the particle size of said ferrochromium and said oxidic columbium material ranging from about 200 to about 400 Mesh by Down and about 100 to about 300 Mesh by Down, respectively, and the molar ratio of oxygen in said oxidic columbium starting material to carbon in said high carbon ferrochromium being maintained in the range from about 1.0 to 1.2; compacting the admixture into a coherent form; heating said coherent

form in vacuo and reacting the carbon in said high-carbon ferrochromium with the oxygen in said oxidic columbium starting material to cause evolution of carbon oxide, the rate of temperature increase during said heating being controlled to maintain the temperature below the eutectic melting point of said coherent form and sufficiently high to cause sintering of said coherent form; continuing said heating to a maximum temperature below about 1500° C. and at a pressure less than about 3 mm. of Hg and until the evolution of carbon oxides substantially subsides; and removing sintered columbium-bearing, low-carbon ferrochromium from the vacuum.

3. A process for producing a sintered, columbium-containing, low-carbon ferrochromium addition agent directly from tin-containing oxidic columbium starting materials and high-carbon ferrochromium comprising admixing a particulate high-carbon ferrochromium, a particulate, tin-containing, oxidic columbium starting material, a binder and at least one particulate sulfur-bearing material selected from the group consisting of the sulfides, said selected sulfur-bearing material having a lower vapor pressure than tin sulphide under operating conditions, the sulfur in said sulfur-bearing material being in amounts sufficient to react with at least about 20 percent of the tin in said oxidic columbium starting material, the particle size of said ferrochromium, said oxidic columbium starting material and said selected sulfur-bearing material ranging from about 200 to about 400 Mesh by Down, about 100 to about 300 Mesh by Down, and about 100 to about 325 Mesh by Down, respectively, and the molar ratio of oxygen in said oxidic columbium starting material to carbon in said high carbon ferrochromium being maintained in the range from about 1.0 to 1.2; compacting the admixture into a coherent form; heating said coherent form in vacuo and reacting the carbon in said high-carbon ferrochromium with the oxygen in said oxidic columbium starting material to cause evolution of carbon oxide and reacting the sulfur in said selected sulfur bearing material with the tin in said tin-containing, oxidic columbium starting material to form a tin sulfide, the rate of temperature increase during said heating being controlled to maintain the temperature below the eutectic melting point of said coherent form and sufficiently high to cause sintering of said coherent form; continuing said heating to a maximum temperature below about 1500° C. and at a pressure less than about 3 mm. of Hg and until the evolution of carbon oxides and vaporization of tin sulfides substantially subsides; and removing sintered columbium-bearing, low-carbon ferrochromium from the vacuum.

4. A process for producing a sintered, columbium-containing, low-carbon ferrochromium addition agent comprising admixing a particulate high-carbon ferrochromium, a particulate oxidic columbium starting material, and a suitable binder, the particle size of said ferrochromium and said oxidic columbium material being about 300 Mesh by Down and about 100 Mesh by Down, respectively, and the molar ratio of oxygen in said oxidic columbium starting material to carbon in said high carbon ferrochromium being maintained at about 1.05 to about 1.15; compacting the admixture into a coherent

form; heating said coherent form in vacuo and reacting the carbon in said high-carbon ferrochromium with the oxygen in said oxidic columbium starting material to cause evolution of carbon oxide, the rate of temperature increase during said heating being controlled to maintain the temperature below the eutectic melting point of said coherent form and sufficiently high to cause sintering of said coherent form; continuing said heating to a maximum temperature below about 1500° C. and at a pressure less than about 3 mm. of Hg and until the evolution of carbon oxides substantially subsides; and removing sintered columbium-bearing, low-carbon ferrochromium from the vacuum.

5. A process for producing a sintered, columbium-containing, low-carbon ferrochromium addition agent directly from tin-containing oxidic columbium starting materials and high-carbon ferrochromium comprising admixing a particulate high-carbon ferrochromium, a particulate, tin-containing, oxidic columbium starting material, a binder and iron sulfide, the sulfur in said iron sulfide being present in amounts sufficient to react with about 20 to 100 percent of the tin in said oxidic columbium starting material and the particle size of said ferrochromium, said oxidic columbium starting material and said iron sulfide material being about 300 Mesh by Down to about 100 Mesh by Down, and about 100 Mesh by Down, respectively, and the molar ratio of oxygen in said oxidic columbium starting material to carbon in said high carbon ferrochromium being maintained at about 1.05 to 1.15; compacting the admixture into a coherent form; heating said coherent form in vacuo and reacting the carbon in said high-carbon ferrochromium with the oxygen in said oxidic columbium starting material to cause evolution of carbon oxide and reacting the sulfur in said selected sulfur bearing material with the tin in said tin-containing, oxidic columbium starting material, to form a tin sulfide, the rate of temperature increase during said heating being controlled to maintain the temperature below the eutectic melting point of said coherent form, and sufficiently high to cause sintering of said coherent form; continuing said heating to a maximum temperature below about 1500° C. and at a pressure less than about 3 mm. of Hg and until the evolution of carbon oxides and vaporization of tin sulfides substantially subsides; and removing sintered columbium-bearing, low-carbon ferrochromium from the vacuum.

References Cited by the Examiner

UNITED STATES PATENTS

2,763,918 9/1956 Megill ---------- 29—182 X

FOREIGN PATENTS

857,752 1/1961 Great Britain.

References Cited by the Applicant

UNITED STATES PATENTS

2,333,573 11/1943 Kalischer.

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