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PROCESS FOR MAKING VANADIUM CARBIDE BRIQUETTES

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ABSTRACT OF THE DISCLOSURE

This invention is a method for producing vanadium carbide useful as a source of vanadium in the manufacture of vanadium containing alloys. The vanadium carbide is prepared by reducing vanadium pentoxide to vanadium tetraoxide which is further reduced to vanadium oxycarbide, adding carbon, briquetting, and vacuum reducing to form the product.

This invention relates to improvements in the manufacture of vanadium-containing alloys and relates in particular to a new and novel process for making vanadium carbide addition materials.

Master alloys or addition alloys for providing the element vanadium to steel in the molten state are conventionally made by reducing vanadium pentoxide. Fused and crushed vanadium pentoxide is a commercially available, relatively pure V_2O_5 that is obtained by the chemical treatment of vanadium bearing ores.

Although commercially available methods for reducing vanadium pentoxide frequently involve the production of an addition alloy known as ferrovanadium, vanadium carbide briquettes, also the product of vanadium pentoxide reduction, are finding increasing use as a vanadium alloy addition source.

The metal vanadium has a high affinity for oxygen and consequently a portion of the vanadium is lost through oxidation when an addition alloy is introduced into molten steel which invariably contains residual oxygen. For many applications the use of the vanadium carbide briquettes is preferred over ferrovanadium because vanadium recovery (percent of vanadium in the addition that actually goes into the alloy) from the use of briquettes is higher. The reasons for the higher recoveries when employing vanadium carbide is attributed to the carbon which is thought to protect the vanadium from oxidation as the alloy goes into solution by preferentially combining with the oxygen present.

Vanadium carbide (82–87% vanadium and 8–15% carbon) may be produced by heating a mixture of vanadium pentoxide and powdered graphite in an electric arc furnace until a semimolten bath is formed. The semimolten bath is permitted to freeze and cool to room temperature while within the furnace crucible. The button of vanadium carbide is then dug out of the crucible, cleaned, crushed, and further cleaned by gravity separation to remove graphitic carbon. This involved procedure produces insufficient vanadium carbode for large commercial use and is primarily employed to produce vanadium carbide for cutting tools.

Commercially available vanadium carbide is produced by direct reduction at high temperatures in substantial vacuums. This procedure requires elaborate vacuum furnace structures capable of withstanding high temperatures for extended periods of time.

We have devised a method whereby fused and crushed vanadium pentoxide may be converted into vanadium carbide briquettes far more efficiently and economically than the prior known methods. Our method combines

heat treatment in gaseous environments and in substantial vacuums in a manner to avoid the undesirable features of the aforementioned methods.

In general, the present invention consists of the following steps:

Step 1.—Crushed and fused V_2O_5 is subjected to a temperature of from about 1050° F. to 1150° F. in a gaseous hydrocarbon reducing atmosphere for sufficient time to reduce the pentoxide to vanadium tetraoxide;

Step 2.—The vanadium tetraoxide is subjected to a temperature of at least 1900° F. in a gaseous hydrocarbon reducing atmosphere so as to convert the tetraoxide to a vanadium oxycarbide;

Step 3.—The vanadium oxycarbide obtained from Step 2 is cooled to ambient temperatures while maintaining the material during cooling in a nonoxidizing environment;

Step 4.—The cooled vanadium oxycarbide is mixed with a carbon source material in amounts to effect a stoichiometric balance of carbon to oxygen within the mixture as to render an excess carbon content when subject to the reaction of Step 6 below which when combined with the vanadium alone consists of from about 8 to about 15% (by wt.) carbon. Preferably, the material is comminuted to a very fine particle size prior to Step 5 herebelow;

Step 5.—Briquetting the mixture of Step 4;

Step 6.—Subjecting the briquettes to a temperature of from about 2500° F.–2700° F. while continuously withdrawing the evolving gases until the evolution of gas substantially stops; and

Step 7.—Cooling the briquettes to substantially ambient temperatures in a nonoxidizing environment.

Our process is not dependent on any one of the aforementioned steps alone but instead provides a superior vanadium carbide briquetted product more efficiently than has been possible heretofore by employing the aforementioned sequence of steps.

The hydrocarbon reducing atmosphere of Step 1 of our process may consist of natural gas, which, though composed largely of methane, consists of a mixture of hydrocarbon gases including propane, butane, etc. Substantially, pure methane, ethane, propane, or butane gases may be employed, however, we have found that a mixture of one or more of these gases is preferred.

Time at temperature of Step 1 is the time required to reduce the V_2O_5 to V_2O_4 at the temperature and in the atmosphere involved. The optimum time to effect a substantially complete reaction is generally from about 60–90 minutes.

It is preferable, though not essential, to continue heating the tetraoxide from the 1050–1150° F. temperature of Step 1 to the 1900° F. temperature of Step 2 while maintaining substantially the same hydrocarbon reducing atmosphere. We have found it to be particularly expedient to perform both of these steps in the externally fired rotating retort type of furnaces when the material is heated to progressively higher temperatures from the end of the furnace in which it is introduced to the end where it is discharged. We preferably position two of these furnaces in tandem so that the furnace of Step 1 discharges into the furnace of Step 2 and the charge is progressively heated to the higher temperatures.

The atmosphere of Step 2, or furnace 2 of the process, is the same as that of Step 1 so that a single elongated externally fired rotating retort furnace may be employed for both Steps 1 and 2.

The temperature of 1900° F. of Step 2 is the minimum practical temperature for accomplishing the desired reaction so that a higher temperature (up to the melting point of the charge) is preferred. Heating equipment

limitations render the temperature range of from 1900° F.–2100° F. the most practical.

The time at temperature for Step 2 varies as in Step 1 but generally a time of from 100 minutes to 180 minutes is sufficient to reduce the V_2O_4 to a vanadium oxycarbide (VC_xO_y where x=0.4 to 0.6 and y=0.4 to 0.8)

The reactions of Steps 1 and 2 can be expressed by the following formulae:

$$V_2O_5+CH_4 \rightarrow V_2O_4+H_2O+CO+CH_4$$
$$V_2O_4+CH_4 \rightarrow VC_xO_y+H_2O+C+CO+H+CH_4$$

We prefer that the vanadium oxycarbide product of Step 2 have a carbon content of 14 to 16%. While the composition of natural gas may be such as to assure this carbon content in the vanadium oxycarbide, it is frequently desirable to add propane gas to the natural gas. An alternate method of assuring a sufficiently high carbon content is to add finely divided carbon with the original V_2O_5 in Step 1, or to add it to the V_2O_4 feed material for Step 2. Coke derived from natural gas has been found effective in raising the carbon content of the VCO with a consequent lowering of the oxygen content.

In Step 3 the vanadium oxycarbide may be cooled while maintaining the reducing atmosphere or while substituting some other nonoxidizing atmosphere.

In Step 4 the vanadium oxycarbide is mixed with a carbon source material in preparation for the reduction of Step 6. The preferred ultimate product is a vanadium carbide that contains from about 8–13% carbon. Vanadium oxycarbide is a homogenous finite material that has a carbon content that can vary from 6 to 22%, but usually varies from 12 to 16%. At the temperature and pressure levels available in commercial vacuum furnaces, about 10% carbon is considered to be an optimum equilibrium point between carbon and oxygen so that in Step 4 there must be a stoichiometric balance between the carbon present and the oxygen content of the vanadium oxycarbide. The total carbon content of the mixture must be such that there is an excess of about 10% carbon over the stoichiometric amount required to combine with the oxygen present in the vanadium oxycarbide.

The carbon source material may be any of the well known carbon rich materials that are disposed to readily yield carbon such as lamp black, graphite, etc.

The mixture must be thoroughly mixed and comminuted to very fine particle size, preferably in a ball mill or rod mill. The comminuted product preferably has a particle size wherein a maximum of about 15% is over 100-mesh and a minimum of 60% will pass through a 325-mesh screen.

In Step 5 the above mixture is agglomerated. Such agglomeration may be accomplished by a great variety of compacting means wherein predetermined quantities of the particulate mass are compressed in such a manner as to effect bodies with sufficient green strength to enable them to be handled for subsequent sintering operations. For example, the mixture may be compacted in a roll type briquetting press. The size of the briquettes produced may be as small as ⅜" x ¾" x ⅜", but preferably are about 1¾" x 1 7/16" x 1" or larger.

In Step 6 the briquettes are heated to within the temperature range of about 2500° F. to 2700° F. in a conventional vacuum furnace. Evolving gases (primarily CO) are drawn off the furnace as fast as possible by the vacuum pumps and the pumps continue to run until the pressure in the furnace drops to a value of less than about 0.050 mm. of mercury. The heating of the furnace is then discontinued.

In cooling the sintered briquettes an inert gas, such as argon, is preferably introduced into the vacuum furnace and the furnace is cooled to yield the desired vanadium carbide sintered product. The sintered briquettes may, of course, be cooled in any appropriate nonoxidizing environment.

In practicing the method of the present invention, vanadium pentoxide previously fused and crushed to the size of 20-mesh and down was charged to an externally heated rotating retort batch type calcining furnace. A flow of natural gas was started through the furnace and the heating of the retort begun. The furnace was held at 1000° F. for a short time before continuing the heating to the maximum temperature. The original purpose of such a hold was to avoid fusion of the pentoxide. Upon reaching the temperature range of 1950° F. to 2050° F. the charge was sampled continuously from the gas exit port.

Analysis of the samples showed an increase in carbon and vanadium contents as the heating continued. When the vanadium reached 70 to 71% and the carbon content 14 to 16%, the heating was discontinued and the charge allowed to cool in the furnace without exposure to air.

Later, the process was carried out in a continuous externally fired rotating retort calcining furnace. With this furnace, the process was carried out in two steps; the fiirst, at about 1100° F. to reduce V_2O_5 to V_2O_4 and the second step at about 2000° F. to reduce V_2O_4 to VC_xO_y. The high production rate made possible by the use of the continuous furnace with natural gas as a reducing agent is a significant part of the present invention.

The pre-reduced product described above was found to be superior to any of the oxides, V_2O_5, V_2O_4, and V_2O_3 as a starting material for the vacuum reduction step. Its higher vanadium content and lower oxygen content required significantly less removal of the carbon monoxide during the vacuum step. A greater number of vanadium units can be charged into a given vacuum furnace using the VC_xO_y as compared with the use of any of the other vanadium oxides used as starting materials. The density of briquettes made with VC_xO_y is greater than that of briquettes made with vanadium oxide. Sintering of the briquettes during the vacuum reduction cycle to obtain a desirable dense product is facilitated by the use of VC_xO_y as an intermediate product.

For commercial production, it has been found to be particularly desirable to employ two externally fired rotating retort calcining furnaces, the first being shorter than the second to accommodate the shorter dwell time for the first step as compared with the second step. The two furnaces are arranged in series so that the product of the first furnace is discharged directly into the second furnace, thus conserving sensible heat. For both furnaces, the feed rate of the charge, the volume of the natural gas flowing countercurrent to the solid charge, the inclination of the rotating retort, the speed of rotation, and the temperature of the furnace are adjusted so that the product discharging from the furnace is of the desired composition. For the first step, the product contains from about 57 to 61% vanadium with less than 0.25% carbon, the balance being largely oxygen with about 1% iron and traces of other impurities. The desired composition of the product from the calcining furnace is as follows: Vanadium, 68–72%; carbon, 14–16%; oxygen, 10–14%.

The oxycarbide of vanadium has been found to be a superior material for the final vacuum reduction step. Prior to this step it is necessary to add additional carbon in some pure form to the pre-reduced product. As stated above, the amount added is stoichiometrically proportional to the carbon and oxygen contents of the oxycarbides. After comminuting to a fine particle size, then compacting to a convenient size, final vacuum reduction is carried out at a temperature in the range of 2500–2700° F. Heating is continued until the carbon-oxygen reaction ceases, that is, when the pressure in the vacuum furnace drops to a low value below 0.050 mm. of Hg.

The oxycarbide product contains significantly less oxygen to be removed by the vacuum treatment than any

of the vanadium oxides. This is illustrated in the following table:

Table I

Product:	Oxygen content, percent
"VCO"	10–14
V_2O_3	32
V_2O_4	39
V_2O_5	45

One object of the vacuum treatment is to remove the oxygen content of the briquetted mixture. This is done through the carbon-oxygen reaction at high temperatures and low pressures to form carbon monoxide which is exhausted through the vacuum pumps. A convenient measure of the extent of this reaction is to determine the weight loss of the product. For complete oxygen removal the following weight losses are shown for the different starting materials, expressed as pounds of gas per ton of charged product. The larger the volume of gas to be removed, the longer the cycle will be, or, the larger the pumping system must be.

Table II

Starting material:	Nominal weight loss=pounds per ton of charged product
"VCO"	420
V_2O_3	790
V_2O_4	950
V_2O_5	1050

It is obvious that the higher the vanadium content and the higher the density of the starting material, the greater the amount of product which can be produced per charge in a given furnace. This is especially significant when viewed from the equipment requirement point of view. As shown in the following table, the furnace volume required for a given production rate is significantly greater for use of any of the oxides of vanadium as starting material, even assuming equal cycle time for the vacuum reduction step.

TABLE III

Starting Material	Relative weight of charged material per pound of V	Relative volume of charged material per pound of V	Density of Charged material, pounds per cu. ft.
"VCO"	1	1	86
V_2O_3	1.22	1.72	61
V_2O_4	1.41	2.24	54
V_2O_5	1.78	3.56	43

Considering the relatively high cost of vacuum furnaces and the amount of depreciation which must be assigned to the cost of producing the product, the economic advantage of using vanadium oxycarbide as a starting material for vacuum reduction is obvious.

It is important that any additive for use in steelmaking have a relatively high density to aid in its solution to molten steel. The degree of sintering during the vacuum reduction determines the density of such products. We have found that higher densities are obtained using vanadium oxycarbide as a starting material for vacuum reduction as compared with products using any of the oxides. Many trials were made under controlled laboratory conditions using optimum particle size of starting materials, optimum briquetting pressures and optimum vacuum treatment conditions. It was found that significantly higher densities were obtained when using vanadium oxycarbide as a starting material. This is illustrated in the following table:

Table IV

Starting material:	Density of vacuum reduced product gms./cc.
"VCO"	4.0–4.5
V_2O_3	3.4–4.0
V_2O_4	3.1–3.6
V_2O_5	2.4–3.0

While we have shown and described the preferred embodiments of our invention, it may be otherwise embodied within the scope of the following claims.

We claim:

1. A method for producing a compacted and sintered vanadium carbide addition alloy from fused and crushed vanadium pentoxide comprising:
   (a) subjecting said pentoxide to a temperature of from about 1050° F. to 1150° F. in a gaseous hydrocarbon reducing atmosphere so as to convert said pentoxide to vanadium tetraoxide;
   (b) subjecting said vanadium tetraoxide to a temperature of at least 1900° F. in a gaseous hydrocarbon reducing atmosphere so as to convert said tetraoxide to vanadium oxycarbide;
   (c) cooling said vanadium oxycarbide to substantially ambient temperatures from said at least 1900° F. in a nonoxidizing environment;
   (d) mixing a carbon source material with said vanadium oxycarbide in amounts to effect a stoichiometric balance of carbon to oxygen within said mixture as to render in the alloy an excess carbon content which when combined with the vanadium content alone consists of from about 8% to about 15% (by weight) carbon;
   (e) briquetting said mixture;
   (f) subjecting said briquettes to a temperature of from about 2500° F. to 2700° F. while continuously withdrawing the evolving gases until the evolution of gas substantially stops; and
   (g) cooling said briquettes to substantially ambient temperatures in a nonoxidizing environment.

2. The method of claim 1 wherein said gaseous hydrocarbon reducing atmospheres of (a) and (b) are composed of the gaseous state of at least one material selected from the group consisting of natural gas, methane, ethane, propane and butane.

3. The method of claim 1 wherein finely divided carbon is added to the vanadium pentoxide prior to Step (a).

4. The method of claim 1 wherein finely divided carbon is added to the vanadium tetraoxide prior to Step (b).

5. The method of claim 1 wherein said 1050 to 1150° F. treatment is conducted for a time of from 60 to 90 minutes and said at least 1900° F. treatment is conducted for a time of from 100 to 180 minutes.

6. The method of claim 1 wherein said carbon source material is added in amounts to effect a stoichiometric balance of carbon to oxygen within said mixture as to render in the alloy an excess carbon content which when combined with the vanadium content alone consists of from about 8% to 13% (by weight) carbon.

7. The method of claim 1 wherein said mixture of carbon source material and vanadium oxycarbide is comminuted to a particle size wherein a maximum of 15% is over 100-mesh and a minimum of 60% will pass through a 325-mesh screen.

8. The method of claim 1 wherein said briquettes are of a minimum size of about ⅜" x ¾" x ⅜".

9. The method of claim 1 wherein said 2500° F.–2700° F. treatment is conducted within a vacuum furnace with the vacuum pumps running to draw off all evolving gases, said treatment continuing until the pressure in the furnace drops to a value of less than about 0.050 mm. of mercury.

10. A method for producing a compacted and sintered vanadium carbide addition alloy from fused and crushed vanadium pentoxide comprising:

(a) heating said pentoxide to a temperature of from about 1050° F. to 1150° F. in a gaseous hydrocarbon reducing atmosphere so as to convert said pentoxide to vanadium tetraoxide;

(b) heating said tetraoxide from said 1050° F. to 1150° F. temperature to a temperature of from about 1900° F. to 2100° F. while maintaining a gaseous hydrocarbon reducing agent so as to convert said pentoxide to a vanadium oxycarbide;

(c) cooling said oxycarbide to substantially ambient temperatures in a nonoxidizing atmosphere;

(d) mixing a carbon source material with said vanadium oxycarbide in stoichiometric amounts to react with the oxygen content of said oxycarbide and in combination with the carbon present in said oxycarbide to render in the alloy a substantially oxygen free vanadium carbide containing from about 8–15% (by weight) carbon;

(e) comminuting said mixture to a particle size wherein a maximum of 15% is over 100-mesh and a minimum of 60% will pass through a 325-mesh screen;

(f) compressing said mixture into briquettes;

(g) heating said briquettes to within a temperature range of 2500° F. to 2700° F. in a vacuum furnace with the vacuum pumps running to remove evolved gases and continuing said treatment until the pressure within said furnace drops to a value of less than about 0.050 mm. of mercury; and

(h) cooling said briquettes in a nonoxidizing atmosphere.

11. The method of claim 10 wherein Steps (a) and (b) are conducted in in-line externally fired rotating retort furnaces wherein the furnace accomplishing Step (a) is disposed for discharge within a nonoxidizing atmosphere into the furnace for accomplishing Step (b).

12. The method of claim 10 wherein Steps (a) and (b) are conducted in a single externally fired rotating retort furnace.

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