United States Patent [19]

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[54] METHOD FOR THE ADDITION OF METALS TO STEEL

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[56] **References Cited**

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[45] Apr. 2, 1974

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[57] ABSTRACT

A process for incorporating a metal in steel by adding to molten iron or steel an intimate mixture, preferably in compacted form, of an oxide of the metal and carbon. The molten iron or steel is at a sufficiently high temperature to initiate a reaction between the carbon and the metal oxide to form, in situ, a metal carbide that readily disperses throughout the molten iron or steel.

9 Claims, No Drawings

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METHOD FOR THE ADDITION OF METALS TO STEEL.

DESCRIPTION OF THE PRIOR ART

The present invention relates to a novel method for incorporating certain metals in steel in order to obtain improved properties of the steel. While the invention is applicable to the incorporation of many metals in steel, such as, for example, chromium, zirconium, titanium, 10 manganese, molybdenum and boron, its greatest utility lies in the inclusion of niobium and vanadium. For this reason, the following description is primarily directed

As is known in the prior art, niobium, when added to steel in small amounts, acts as a ferrite grain refiner and promotes strengthening of the steel. Vanadium also 20 strengthens steel, probably by a solid solution hardening mechanism, resulting in a refinement of the ferrite grain size.

Niobium and vanadium are conventionally added to molten steel in the form of a ferro-alloy that is pro-25 duced by smelting an oxide or ore of the metal with aluminum or silicon in the presence of iron. This smelting process is expensive in its use of aluminum or silicon reducing agents and is rather inefficient as only about 85 percent to 90 percent of the niobium or vanadium 30 charged to the smelter can ordinarily be recovered as a useful ferro-alloy.

It is also known to mix niobium or vanadium with molten steel while they are in the form of their respective carbides. Several processes are known to produce 35 the carbides in which the oxide or ores of the metals are reacted with carbon at elevated temperatures (that is, generally above 1,400° C). To obtain high purity (that is, less than about 2 percent residual oxide), it is necessary to conduct the reaction in a nonoxidizing atmo- 40 trine or the like, can also be extruded to form comsphere either by using a vacuum chamber or by circulating a noble gas. In either case, the gaseous reaction products are removed from the reaction zone to drive the reaction to completion. In addition to being expensive and somewhat complex, these processes are com- 45 metric amount of carbon theoretically required to proparatively slow and may take many hours at the elevated temperature to obtain a desired degree of purity.

I have now devised a method for adding niobium or vanadium to molten steel which is characterized by the 50 use of inexpensive reagents, simple equipment and high recovery and utilization of the niobium or vanadium. Further, the present invention eliminates the need to reduce niobium or vanadium oxide to a metal or metal carbide before their addition to the molten steel, thus ⁵⁵ avoiding the use of high temperatures, controlled atmospheres and expensive reagents.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a simple method for the incorporation of certain metals, such as niobium or vanadium, into steel.

Another object of this invention is to provide a process in which ores and oxides of metals such as niobium and vanadium can be mixed with molten steel without first converting these materials to a ferro-alloy or a carbide form.

A further object of this invention is to provide a method for the introduction of certain metals such as niobium or vanadium into low alloy steels, which processes maximize the efficient utilization of the metals.

These and other objects of this invention are achieved by forming an intimate mixture of carbon and an oxide or ore of a metal and adding the mixture to molten steel. Preferably, for ease in handling, the mixture is compacted and formed into a briquet or pellet prior to its addition to the molten steel.

DESCRIPTION OF THE INVENTION

In the practice of the present invention, niobium stood that the invention is not intended to be so limited. ¹⁵ oxide or vanadium oxide or ores containing one of these match and the mixed with finely divided carbon. The carbon is sized -100 and preferably -200 mesh and finer. The blending of the metal oxide and carbon can be suitably accomplished using a muller, double-cone or twin-cone type of blender. Additionally, if desired, finely divided iron powder suitably sized to 35 mesh and finer may be blended with the metal oxide and carbon. The presence of the iron powder in the product leads to increased strength and density of the compact. The iron powder can be added in amounts of between 10 percent and 90 percent by weight of the mixture.

The blend of metal oxide and carbon, with or without iron powder, is preferably compacted by standard means as into a briquet. The compaction can be accomplished using a mechanical press, a continuous double-roll press, an isostatic press, or other similar device. Generally, it is advantageous to include a binding agent in the mixture such as methyl cellulose or other carbonaceous binding material. The use of a pelletizing disc or drum can also be employed, but the resulting pellet will be less dense. The blend, if wetted and provided with a suitable binding agent such as sugar, dexpacts.

In preparing the reaction mixtures in accordance with the present invention, it is desirable to add at least 90 percent, and preferably 100 percent, of the stoichioduce the desired carbide. The stoichiometric amount of carbon can be calculated from the following general equations:

$$Nb_2O_5 + 7C = 2NbC + 5CO$$

(1)

$$V_{2}O_{5} + 7C = 2VC + 5CO$$

(2)

$$V_2O_5 + 6C = V_2C + 5CO$$

(3)

$$V_2O_3 + 5C = 2VC + 3CO$$

(4)

$$V_2O_3 + 4C = V_2C + 3CO$$

(5)

It will be understood that carbon in excess of that amount stoichiometrically required may be used, but the excess

It of carbon will merely dissolve in the molten steel and will increase the carbon content of the steel. Thus, if 5 desired, a stoichiometric excess carbon may be used for the purpose of obtaining a final adjustment of the carbon content of the steel. If the ores of niobium or vanadium are used instead of pure oxides, additional carbon must be added to convert other reducible species pres-10 ent in the ore to their respective metals or carbides.

The metal oxide-carbon compacts can be added to molten steel either in the ladle or in the mold. The compacts disperse readily into the molten steel and produce an equivalent effect as a ferro-alloy added to the steel. 15

The following examples are illustrative of the practice of the invention. Mesh sizes referred to are Tyler Screen Size Series.

EXAMPLE I

Niobium oxide (Nb_2O_5) sized to -100 mesh in the amount of 50 grams and 15.8 grams carbon black (Thermax Carbon) sized to -200 mesh plus 25 grams iron powder sized to -35 mesh were blended and compacted in a mechanical press at 20,000 psi (pounds per square inch). The compact was about 1/2-inch thick by 1 inch in diameter. The compact was added to 10 pounds of molten steel at 1,600° C. The compact completely dispersed in the steel without agitation in about 30 3 minutes. The steel was cast into an ingot and was found to contain 0.73 percent niobium for an indicated 95 percent recovery of the niobium. Metallographic examination of the ingot showed uniform disperson of the niobium carbide. 35

EXAMPLE II

Araxa pyrochlore, as received, in the amount of 25 grams was blended with 10 grams of carbon black sized to -200 mesh plus 3 grams methyl cellulose and com- 40 pacted in a mechanical press at 20,000 psi. The compact was added to 10 pounds of molten steel at 1,600° C. The compact dispersed into the molten steel without agitation in about 2 minutes. The steel was cast into an ingot and was found to contain 0.18 percent niobium 45 for an indicated 95 percent recovery of niobium. The niobium carbide was evenly dispersed throughout the alloy.

EXAMPLE III

St. Lawrence pyrochlore, ground to -100 mesh, in the amount of 25 grams was blended with 8 grams of carbon black sized to -200 mesh plus 3 grams methyl cellulose and compacted in a mechanical press at 20,000 psi. The compact was added to 10 pounds of 55 molten steel at 1,600° C. The compact dispersed into the molten steel without agitation in about 2 minutes. The steel was cast into an ingot and was found to contain 0.17 percent niobium for an indicated recovery of 90 percent. The niobium carbide was evenly dispersed 60 throughout the alloy.

EXAMPLE IV

Vanadium pentoxide (V_2O_5), sized to -100 mesh, in the amount of 25 grams was blended with 10.5 grams carbon black sized to -200 mesh and compressed into a pellet in a mechanical press at 30,000 psi. The compact was added to 10 pounds of molten steel at 1,600° C. The pellet took about 2 minutes to dissolve in the steel without agitation. The steel was cast into an ingot and was found to contain 0.30 percent vanadium for an indicated recovery of 98 percent.

The foregoing examples illustrate how niobium or vanadium oxide, either as ores or pure oxides, and carbon can be added to molten steel to produce niobium or va-¹⁵ nadium carbide in situ. The process is advantageous in that it avoids the expensive pretreatment of the oxides or ores in the reduction process currently employed; it provides for a uniform dispersion of the metal throughout the steel; and it makes possible the efficient utiliza-²⁰ tion of the metal.

I claim:

1. A process for incorporating a metal in steel which comprises introducing an intimate mixture of a finely divided material containing the metal substantially in oxide form and a finely divided carbon into molten steel.

2. A process according to claim 1 wherein the metal is niobium, vanadium, chromium, zirconium, titanium, manganese, molybdenum or boron.

3. A process according to claim 1 wherein the temperature of the molten steel is sufficiently high to initiate a reaction between the oxide of the metal and the carbon to form, in situ, a carbide of the metal.

4. A process according to claim 3 wherein sufficient carbon is included in the mixture to approximate at least the stoichiometric amount required to obtain complete conversion of the metal oxide to its metal carbide form.

5. A process according to claim 4 wherein final adjustment of the carbon content of the steel is obtained by adding carbon to the mixture in excess of the stoichiometrically required amount.

6. A process according to claim 1 wherein the material containing an oxide of the metal is -65 mesh.

7. A process according to claim 1 wherein the carbon is -100 mesh.

8. A process according to claim 1 wherein between 10 percent and 90 percent by weight of a -35 mesh $_{50}$ iron powder is included in the mixture.

9. A process for the production of high-strength, lowalloy steel which comprises adding to molten iron or steel an intimate mixture of a metal substantially in oxide form oxide selected from the group consisting of niobium oxide, vanadium oxide, chromium oxide, zirconium oxide, titanium oxide, manganese oxide, molybdenum oxide, boron oxide, and ores containing these oxides, and a sufficient quantity of carbon to enable the conversion of the metal from its oxide to its carbide form.

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