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## VANADIUM-CONTAINING ALLOYING ADDITIVE FOR STEEL

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7 Claims

### ABSTRACT OF THE DISCLOSURE

Vanadium-containing alloying additive for steels is obtained from vanadic acid, i.e., vanadium pentoxide or vanadium pentoxide-containing compositions in a one stage process without the use of vacuum treatment by the solid-state reduction of vanadic acid with carbon under atmospheric conditions at temperatures of from 1200 to 1500° C., to produce a substance of the following composition:

	Percent, from—
Vanadium	70 to 85
Oxygen	2 to 10
Carbon	5 to 20
Nitrogen	0.5 to 4

To take up residual oxygen in a steel-making bath into which said additive is added, silicon or aluminum or a ferrosilicon may be incorporated in the additive.

The use of such an additive in a steel making process is particularly advantageous in that the additive dissolves well in the steel bath despite residual oxygen in the steel making bath. The high density of the additive results in it taking up a position in the steel bath between the slag and the bath surface, thereby effecting a further improvement in solution.

This invention relates to a vanadium-containing substance produced in a one-stage reduction process, which is useful as an alloying agent for steel production.

It is known to alloy steel with vanadium by adding to the steel bath ferrovanadium having a vanadium content in the range of from 50 to 80% thereof. It is also known to add the vanadium in the form of carbon-containing ferrovanadium containing from 3 to 10% of carbon, the vanadium being combined therein in the form of carbide. It has recently become known that a vanadium carbide ( $V_2C$ ) produced in the solid state can be used as an alloying agent. It is claimed that this product has the advantage of greater economy in comparison with ferrovanadium, which is produced by the aluminothermal reduction of vanadium pentoxide. Nevertheless its production is expensive and time-consuming, several process stages being required to produce the  $V_2C$ . Thus, in the first stage, vanadium pentoxide or ammonium vanadate is reduced to vanadium trioxide, which, with the corresponding quantity of carbon, is then reduced to vanadium carbide under reduced pressure over a long period at a temperature between 1200 and 1400° C.

The invention provides a process whereby a vanadium-containing alloying additive derived from vanadic acid, i.e., vanadium pentoxide or a composition containing a major proportion of vanadium pentoxide, which is useful as an alloying agent for steel production, can be produced in one stage and without vacuum treatment directly from vanadic acid compounds. One such compound is vanadium pentoxide itself, which on an industrial scale is pre-

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cipitated from a sodium vanadate solution, dried, calcined or melted, the product containing impurities (which may amount to up to 10% individually or together) such as alkali and ammonium induced in the precipitate stage. Another such compound is ammonium metavanadate, which decomposes at a temperature in excess of 100° C. with the liberation of ammonium salts of vanadium pentoxide or vanadium pentoxide associated with lower-valency oxides.

The invention consists of a vanadium-containing substance, useful as an alloying additive for steels, which is produced in the solid-state reduction of vanadic acid with carbon under atmospheric conditions at temperatures of 1200–1500° C., having a composition:

	Percent, from—
Vanadium	70 to 85
Oxygen	2 to 10
Carbon	5 to 20
Nitrogen	0.5 to 4

The term "carbon" used in the said composition includes compounds such as carbon black, charcoal, coal, coke and electrode coke.

The vanadium-containing substance thus obtained dissolves easily in steel baths, despite the residual oxygen content. Reaction between carbon and oxygen takes place in the steel bath, the CO containing gases thus generated causing agitation of the melt leading to improved distribution of the vanadium throughout the steel. This is particularly important due to the small proportion of vanadium used as an alloying material.

The alloying agent according to the invention is obtainable in the form of briquettes or pellets, or a porous sinter, which can be added directly to the steel bath.

To facilitate the reaction of the residual oxygen being effected in the steel bath, it may be advantageous to incorporate a further reducing agent in the alloying agent, for example silicon and/or aluminium, which may be in the form of a known ferro alloy, such as ferro silicon, ferro aluminium or ferro silicon aluminium. Carbon may also be incorporated at the same time.

The additions of silicon and/or aluminium and possibly carbon must, of course, be such that they are only enough to reduce the residual oxygen and do not cause impermissible carburisation or an undesirable increase in these contents in the steel bath.

The alloying agent according to the invention may be introduced into the steel bath in comminuted form, in metal or combustible containers, for example tin boxes, or bags of paper or of plastics material or the like. If desired it may also be blown into the bath using known techniques.

Briquettes of the alloying agent may be obtained using known techniques of briquetting. The briquettes thus obtained are of high density and which is greater than the density of conventional slags, so that they lie between the bath slag and the bath surface during solution which assists the act of solution.

The following examples of the invention are provided:

#### EXAMPLE 1

100 kg. of industrial vanadic acid containing 84.8% of  $V_2O_5$  and 4.5% of  $H_2O$ , the remainder being precipitation-induced impurities; and 30 kg. of fine coke containing 91% of carbon in the dried state and 3.4% of  $H_2O$ ; were mixed with about 10% of water to prevent dust loss, and kernel oil was added as a binder. Pellets of from 4 to 6 mm. diameter were formed from this mixture on a pelletising dish with the addition of more water. The pellets were then put in the reduction furnace and calcined for six hours at 1350° C. The reducing atmosphere was obtained by covering the pellets with granulated coke. To prevent the entry of air, closed clay graphite crucibles

were used, the crucibles passing through a tunnel furnace. With a charge of 125 kg. of pellets (dry) there were obtained 64.5 kg. of alloying agent containing 73.2% of vanadium, 16.5% of carbon, 1.8% of oxygen and 2.0% of nitrogen, the remainder consisting of impurities, being ash components of coke.

The apparent density of these pellets was 0.71 kg./dm.<sup>3</sup>. After comminution and pressing into briquettes, the density was from 3 to 3.4 kg./dm.<sup>3</sup>.

#### EXAMPLE 2

Pellets of a vanadium product containing less carbon than that obtained in Example 1, was produced in the same way as Example 1, from 100 kg. of vanadic acid and 22.5 kg. of coke.

60 kg. of final product contained 79.2% of vanadium, 6.9% of carbon, 6.1% of oxygen and 2.9% of nitrogen.

This product contained too much oxygen in relation to the carbon content, and an alloying agent was prepared from the said product by admixing therewith 5.3 kg. of pulverised 75% ferrosilicon and pressing into briquettes with kernel oil binder, the briquettes having a density of 3.1 kg./dm.<sup>3</sup>.

The alloying agent contained 72.8% of vanadium, 6.3% of carbon, 6.1% of silicon, 2.5% of iron, 5.6% of oxygen and 2.7% of nitrogen.

The briquettes prepared according to Examples 1 and 2 were added to steel baths having a temperature of 1580° C. After two to three minutes the briquettes dissolved and a uniform distribution of the 0.15% of vanadium was achieved in the steel bath, corresponding to a vanadium take up of over 90%.

The absence of the use of expensive reduced pressure stages in preparing the alloying agents according to the invention means that the cost of preparation is reduced, and the frequent repair of reduced-pressure apparatus owing to the high temperatures used, is avoided. The reaction times required for the production of the agent according to the invention are, moreover, much shorter, and the production of the alloying agent is not restricted to the use of any particular type of furnace. All that is required is that the reaction temperatures can be reached and the calcination material can be subjected to a reducing atmosphere. Thus, for example, reducing rotary tubular kilns or continuously-burning furnaces may be used.

What is claimed is:

1. A vanadium-containing alloying additive for steels, obtained by the solid-state reduction of vanadic acid with carbon under atmospheric conditions at a temperature in the range 1200–1500° C., the said alloying additive having a composition;

Percent, from—

Vanadium	70 to 85
Oxygen	2 to 10
Carbon	5 to 20
Nitrogen	0.5 to 4

2. A vanadium-containing alloying additive as claimed in claim 1, containing at least one reducing agent selected from the class consisting of silicon, aluminum, ferrosilicon, ferroaluminum and ferrosilicon aluminum.

3. A process of preparing an alloy steel bath, and incorporating in the said steel bath a vanadium-containing alloying additive having a composition:

Percent, from—

Vanadium	70 to 85
Oxygen	2 to 10
Carbon	5 to 20
Nitrogen	0.5 to 4

4. A process according to claim 3, in which the said vanadium-containing alloying additive contains a reducing agent selected from the class consisting of silicon, aluminum, ferrosilicon, ferroaluminum and ferrosilicon aluminum.

5. A process according to claim 3, in which the said vanadium-containing alloying additive is added to the said steel bath in the form of a pressed mass selected from the class consisting of briquettes, pellets and porous sinter.

6. A process according to claim 3, in which carbon is incorporated in the said steel bath in addition to the said vanadium-containing alloying element, in a proportion sufficient to effect reduction of residual oxygen in the said steel bath.

7. A process according to claim 3, in which the said vanadium-containing alloying additive is added to the said steel bath in comminuted form contained in a container.

#### References Cited

##### UNITED STATES PATENTS

1,119,643	12/1914	Saklatwalla	75—133
1,697,759	1/1929	Feild	75—133
1,811,698	6/1931	Saklatwalla	75—133
1,901,367	3/1933	Gustafsson	75—133.5
2,381,675	8/1945	Linz	75—133X
2,576,763	11/1951	Linz	75—133

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