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NITROGEN-CONTAINING ALLOY AND
ITS PREPARATION

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The present invention relates to a novel nitrogen-containing alloy and to its preparation; and, more particularly, it relates to an alloy containing, as its principal constituents, nitrogen, manganese and vanadium which alloy is especially adapted for use in the manufacture of steel which is to contain nitrogen and one or more of the other elements.

In the manufacture of steel containing nitrogen and manganese it has been proposed to add these elements in the form of a nitrogen-manganese alloy prepared by nitriding manganese or ferromanganese. According to Patent 2,696,433, when ferromanganese is nitrided, the nitrogen content will not be greater than 5%. In practice, the nitrogen content has been found to be much less than 5%, particularly when low- or medium carbon ferromanganese is employed. With relatively pure electrolytic manganese the maximum nitrogen content is only about 7% according to the aforementioned patent, and is somewhat lower in practice. If vanadium is also desired, this element could be added, along with the nitrided manganese, as ferrovanadium. However, this requires a separate addition of material. On the other hand, vanadium nitride, formed by the thermal decomposition of ammonium vanadate is known as an abrasive material. Although this may contain about 20% of nitrogen, its melting point is far too high for addition to steel melts as a source of either vanadium or nitrogen.

It is the principal object of the present invention to provide a novel nitrogen-containing alloy.

Another object of the invention is to provide an alloy comprising nitrogen and manganese which can contain up to about 17% of nitrogen.

Still another object of the present invention is to provide an alloy comprising nitrogen and vanadium and which is suitable for addition to molten steel in the preparation of steels containing nitrogen and vanadium.

A further object of the invention is to provide an alloy containing, as its principal constituents, nitrogen, vanadium and manganese which can contain substantial amounts of nitrogen and can be added to molten steel as aforesaid and which can also be prepared using ferromanganese as the source of manganese.

Other objects, including the provision of a method of making the novel alloy and the use of the novel alloy in preparing alloy steels, will become apparent from a consideration of the following specification and the claims.

The novel alloy of the present invention consists essentially of from about 50 to about 75% of vanadium, from about 5 to about 25% of manganese and from about 6 to about 17% of nitrogen, said percentages being by weight based on the weight of the alloy. As will appear hereinafter the alloy will also contain from trace to small amounts of other elements, the amount and type depending upon the extent of their presence in the materials used in preparing the alloy.

The novel alloy is prepared by nitriding an alloy consisting essentially of from about 70 to about 80% of vanadium and from about 17 to about 27% of manganese, as by contacting said alloy, in finely-divided form and at an elevated temperature, with nitrogen gas until the resulting alloy contains from about 6 to about 17% of nitrogen based on the weight of the nitrogen-containing

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alloy. The resulting alloy is advantageously reduced to finely-divided form and compressed, with the aid of a binder, into discrete bodies like briquettes.

The base vanadium-manganese alloy which is nitrided according to the present invention is prepared by melting together vanadium and manganese in the proportions stated above. The manganese may be supplied through the use of electrolytic manganese, ferromanganese or silicomanganese. Silicomanganese consists principally of from about 67 to about 70% of manganese and from about 16 to 25% of silicon depending upon the amount of carbon present which may range up to 2.5%, the balance being principally iron with small amounts of other impurities like phosphorus and sulfur. To the extent silicomanganese is used as a source of manganese, the resulting base alloy which is to be nitrided will contain silicon and this may range up to about 8% by weight of the alloy. The preferred source of manganese is ferromanganese and the use of this material will introduce iron to the resulting alloy which is to be nitrided and this may range up to about 10% by weight of the alloy. Low-, medium- or high-carbon ferromanganese may be used. While the vanadium may be supplied by various vanadium-containing materials, like vanadium-bearing slags and vanadium residues, the preferred source of vanadium is vanadium pentoxide (V_2O_5) which will be reduced to vanadium. This reduction is advantageously accomplished with aluminum. Hence, the well-known aluminothermic process may be used in preparing the base alloy and, as a result, aluminum will be present in the alloy in amounts up to about 4% by weight of the base alloy. Reduction of vanadium pentoxide can also be accomplished by the conventional carbon reduction method, in which case heat is supplied externally. Reference has been made above to the presence of silicon, iron and aluminum in the base alloy to be nitrided. Normally there will be at least a trace amount of each of these elements present.

In preparing the base vanadium-manganese alloy by the aluminothermic process, the source of manganese, the vanadium pentoxide and aluminum are mixed in the desired ratio and ignited. Oxidation of the aluminum, by reduction of the vanadium pentoxide, generates heat and this is sufficient to melt the constituents. In preparing the base alloy by carbon reduction, the source of manganese and the vanadium pentoxide may be heated together in a carbon arc furnace. The molten alloy is cooled to solidify it, and the slag is removed. The alloy is ground to finely-divided form in preparation for nitriding. Generally, the alloy is ground sufficiently so that substantially all thereof passes through a 10 mesh screen, and preferably through a 50 mesh screen.

In accordance with the present invention, the base vanadium-manganese alloy is nitrided. This comprises contacting the base alloy, in finely-divided form, with gaseous nitrogen at an elevated temperature at which nitrogen combines with the vanadium and manganese. The nitriding reaction begins at about 700° C., and the rate increases as the temperature rises until the optimum rate is at temperatures from about 900° C. to about 1100° C. Since melting of the alloy is not desirable, the maximum temperature employed will be below the melting point of the alloy being nitrided. Generally, the temperature will not exceed about 1200° C.

Contact of the base alloy with nitrogen will continue until the desired amount of nitrogen has been combined with the alloy. This can be determined empirically or through measurements of the gas consumed. In general, it is a matter of hours. For example, at the preferred temperature range of about 900° C. to about 1100° C. the time required is from about 4 to about 8 hours.

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Following the procedure described above, nitrogen-containing alloys may be prepared having the following analyses in which the figures given are approximate and represent percent by weight.

	General Range	Preferred Range
V	50-75	55-65
Mn	5-30	10-25
N ₂	6-17	10-15
Fe	Trace-8	.1-5
Al	Trace-1	.5-1
Si	Trace-6	.5-1
C	Trace-3	.1-1

The resulting nitrogen-containing alloy, while suitable for use as such, contains fines which are difficult to immerse in the molten steel. For this reason it is preferred to compress the material, after reduction to finely divided form if necessary, into bodies, like briquettes. Hence, the nitrogen-containing alloy, ground to through 10 mesh, preferably through 60 mesh, may be mixed with a binder and briquetted. The nature of the binder is not critical, and it may be organic, like molasses, or inorganic, like sodium silicate, or both, like a mixture of molasses and lime. Conventional briquetting practice may be followed in the selection of binder and briquetting procedure, as well as in the selection of the amount of binder which may range from about 2 to about 10% by weight of the alloy.

The nitrogen-containing alloy is especially adapted for addition to and dissolving in molten steel in the preparation of steel containing nitrogen and vanadium and/or manganese. The present alloy may be added to the steel in an amount from about 0.4 to about 4 pounds per ton of steel depending upon the concentration of the elements desired in the final steel. In this connection, it will be clear that the present alloy need not be the sole source of the three elements, since adjustment may have to be made in particular instances. For example, a given alloy of the present invention may provide the desired level of nitrogen and of manganese but not quite the desired level of vanadium. In this case, another source of vanadium, like ferrovanadium, may be added along with the alloy to make the necessary adjustment.

The present invention will be more readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way.

Example I

Vanadium pentoxide, electrolytic manganese and aluminum are mixed and ignited according to conventional aluminothermic procedure to provide a vanadium-manganese alloy having the following analysis:

	Percent
V	72.6
Mn	22.5
Fe	2.9
Si	1.38
Al	.20
C	.02

The alloy is ground to through 50 mesh and is placed in a sintered alumina crucible. The alloy is preheated to 600° C., and nitrogen gas is flowed thereto from a tube extending to the bottom of the crucible. While nitrogen is being added the temperature of the alloy is increased at the rate of 100° C. every hour until the temperature reaches 1200° C. The nitriding reaction begins at about 700° C. and by the time 900° C. is reached the rate has increased considerably. At 1100° C. very little further nitrogen consumption occurs. After 8 hours from the starting of preheating, which includes 45 minutes for preheating to 600° C., the flow of nitrogen is stopped and heating is discontinued.

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The resulting alloy, in the form of a sintered mass containing coarse and fine particles, has the analysis:

	Percent
V	61.34
Mn	20.60
N ₂	14.50
Fe	1.70
Si	.78
Al	.07
C	.01

The alloy is added as such, in the amount of two lbs. per ton of steel, to molten steel to provide a steel having the analysis: 1.25% max. Mn; 0.02% min. V; 0.15% max. N₂; 0.22% max. C; 0.05% max. S, and 0.04% max. P.

In two different heats the alloy provided the following recoveries and contents of vanadium and nitrogen:

	Recoveries	Contents
Heat #1	80.7% V and 64.5% N ₂	0.013% N ₂ and 0.050% V.
Heat #2	75.76% V and 63.95% N ₂	0.014% N ₂ and 0.060% V.

In a third heat, 0.33 lbs. of ferrovanadium per ton of steel are added to provide 0.012% N₂ and 0.070% V.

Example II

Twenty four hundred pounds of low alkaline vanadium pentoxide, 1180 lbs. of aluminum and 250 lbs. of medium carbon ferromanganese are mixed and ignited according to conventional aluminothermic practice. The resulting alloy has the approximate analysis:

	Percent
V	79
Mn	14.5
Fe	3
Al	0.14
Si	0.7
C	0.3-0.4
S	0.02

The alloy, after grinding to a powder, is placed in stainless steel tubes held in a carburizing furnace and preheated to 900° C. Nitrogen gas is then introduced to the bottom of each tube for periods of time ranging from 4 to 8 hours for different tubes. In this way nitrided alloys are produced having nitrogen contents ranging from about 6 to about 16%.

One such alloy, containing V-57.91%; Mn-15.23% and N₂-8.82%, is ground to through 60 mesh and mixed with a mixture of 8 pts. molasses and 2 pts. lime. The mixture is then compressed into briquettes.

The alloy briquettes are added to molten structural vanadium steel in the amount of 325 lbs. per 150 tons of steel. This provides, in the final steel, vanadium and nitrogen contents of 0.039% and 0.009%, respectively, for percent recoveries of 80% vanadium and 93% nitrogen, respectively.

Modification is possible in the selection of raw materials for preparing the alloy as well as in the techniques and procedures employed without departing from the scope of the invention.

What is claimed is:

1. A nitrogen-containing alloy consisting essentially of from about 50 to about 75% of vanadium, from about 5 to about 30% of manganese and from about 6 to about 17% of nitrogen.
2. The alloy of claim 1 containing up to 8% of iron.
3. The alloy of claim 1 containing up to 1% of aluminum.
4. The alloy of claim 1 containing up to 6% of silicon.

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5. A nitrogen-containing alloy the analysis of which is as follows:

V	From about 50 to about 75%.
Mn	From about 5 to about 30%.
N ₂	From about 6 to about 17%.
Fe	Trace to about 8%.
Al	Trace to about 1%.
Si	Trace to about 6%.
C	Trace to about 3%.

6. A nitrogen-containing alloy consisting essentially of from about 55 to about 65% of vanadium, from about 10 to about 25% of manganese and from about 10 to about 15% of nitrogen.

7. The alloy of claim 6 containing up to about 5% of iron.

8. The alloy of claim 6 containing up to about 1% of aluminum.

9. The alloy of claim 6 containing up to about 1% of silicon.

10. A nitrogen-containing alloy the analysis of which is as follows:

V	From about 55 to about 65%.
Mn	From about 10 to about 25%.
N ₂	From about 10 to about 15%.
Fe	From about 0.1 to about 5%.
Al	From about 0.5 to about 1%.
Si	From about 0.5 to about 1%.
C	From about 0.1 to about 1%.

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11. The method of preparing an alloy which comprises nitriding a vanadium-manganese alloy consisting essentially of from about 70 to about 80% of vanadium and from about 17 to about 27% of manganese until the resulting alloy contains from about 6 to about 17% of nitrogen.

12. The method of claim 11 wherein said vanadium-manganese alloy contains up to about 10% of iron.

13. The method of claim 11 wherein said vanadium-manganese alloy contains up to about 4% of aluminum.

14. The method of claim 11 wherein said vanadium-manganese alloy contains up to about 8% of silicon.

15. The method of claim 11 wherein said vanadium-manganese alloy, while in finely-divided form, is contacted with nitrogen gas at a temperature of at least 700° C. and below the melting point of the alloy.

16. The method of claim 15 wherein the temperature during nitriding is from about 900 to about 1100° C.

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