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3,385,696

PROCESS FOR PRODUCING NICKEL-MAGNESIUM PRODUCT BY POWDER METALLURGY

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5 Claims. (Cl. 75—130)

The present invention is directed to the production of
nickel-magnesium agents particularly adapted for the
purpose of introducing magnesium into molten cast iron
and, more particularly, to a powder metallurgy method for
the production of such agents.

In recent years the introduction of magnesium into
molten iron has come to be widely practised, both for the
production of spheroidal graphite cast iron, in which the
graphite is rendered spheroidal by means of retained mag-
nesium, and for other purposes. It is now well known that
to ensure that the graphite formed in cast iron, either on
solidification or during a graphitizing heat treatment, is
spheroidal, generally requires a retained magnesium content
of up to about 0.1%, e.g. 0.04 to 0.08%.

The utility of an addition material for introducing mag-
nesium into molten iron may be measured in terms of its
"efficiency," defined as follows:

Efficiency (%) =

$$\frac{\text{Mg recovery (\%)} \times \text{Mg content of alloy (\%)}}{100}$$

where

Mg recovery (%) =

$$\frac{\text{Residual Mg (\%)} + 3/4 (\text{Initial sulfur (\%)}) \times 100}{\text{Mg added (\%)}}$$

Magnesium cannot be introduced as such into molten
iron because of the violence of the reaction that takes
place, and the regular practice is to introduce it as an
alloy with another metal. All the alloys commonly used
for the purpose are made by melting, and the production
of the alloys in this way is very troublesome. Invariably
some of the magnesium and other metals is lost in the
process; it is impossible to exclude dross and inclusions
from the alloys; the magnesium in the alloys tends to
segregate so that the composition of the alloys is not
constant; and the alloys when formed have to be broken
into small pieces before they can be added to molten iron.
In the course of the breaking, substantial amounts of the
alloys are lost as a result of the production of unusable
fine particles. Despite all these disadvantages, alloys made
by melting are those regularly used.

Of these alloys formed by melting, those of nickel and
magnesium afford certain advantages, and in particular
nickel is extremely effective in moderating the violence of
the reaction between magnesium and molten iron. More-
over it is often a very useful constituent of the cast iron
formed. The standard nickel-containing alloy in use con-
tains from 14 to 16% magnesium. This alloy has many
advantages. In particular, its reaction with molten iron,
though spectacular, is not violent; and its density is greater
than that of the molten iron so that it sinks into the melt
and remains submerged during reaction.

Nickel-magnesium alloys containing a higher propor-
tion of magnesium have lower densities than the 15%
magnesium alloy, and to avoid excessive losses of mag-
nesium they need to be held below the surface of the melt
by a plunger while they react with the molten iron. When
they are added by plunging, the efficiency of such nickel-

magnesium alloys is high, and generally higher than that
obtained by a direct addition of the standard 15% mag-
nesium alloy. Nevertheless these high-magnesium alloys
are not used to any great extent, largely because they are
very difficult to produce commercially by melting tech-
niques. Melting losses are high, and segregation of magne-
sium in the cast nickel-magnesium ingots readily occurs.

Various proposals have also been made to produce
magnesium-containing addition agents by compacting
magnesium powder with other powders, with or without
subsequent sintering of the compacts. When the compacts
are added as such to the molten iron, the magnesium is
inadequately protected from the iron, and the magnesium
recovery and efficiency both tend to be low. When the
compacts are sintered, there is loss of magnesium during
the sintering, with resultant difficulties in controlling the
composition of the addition agent.

We have now discovered a method for producing nickel-
magnesium addition agents by powder metallurgy which
overcomes the aforementioned problems and provides
agents which are metallurgically clean, which can be pro-
duced in bodies of regular, controllable size, weight and
magnesium content and which are effective addition agents
for the purpose of introducing magnesium into molten
cast iron even when the magnesium content thereof is sub-
stantially higher than that which has been heretofore gen-
erally accepted as being tolerable on a practical level.

It is an object of the present invention to provide a
powder metallurgy method for the production of nickel-
magnesium bodies particularly useful for the introduction
of magnesium into molten cast iron.

It is another object of the present invention to provide
a method for producing nickel-magnesium bodies by
powder metallurgy which are metallurgically clean and
which have a controlled substantially uniform magnesium
content.

Still another object of the present invention is to pro-
vide by powder metallurgy nickel-magnesium bodies hav-
ing improved addition characteristics when employed to
introduce magnesium into molten cast iron.

It is a further object of the present invention to produce
by powder metallurgy improved nickel-magnesium bodies
of controlled size and weight which enable calculation of
desired magnesium additions simply by counting the
quantity of nickel-magnesium bodies to be employed.

Other objects and advantages of the invention will be-
come apparent from the following description.

We have found that useful nickel-magnesium addition
agents can be prepared without melting from particles of
magnesium coated with nickel. Our invention comprises
compacting together particles of nickel-coated magnesium
powder with or without other particles in a proportion
such that the magnesium constitutes from 10 to 50%
of the compacts by weight. Higher proportions of mag-
nesium lead to undesirably violent reaction with molten
iron and low recoveries of magnesium, while if the mag-
nesium content is less than 10% such a large proportion
of the addition agent must be added to the iron to intro-
duce a given amount of magnesium as undesirably to
lower the temperature of the molten iron, and also un-
necessarily to increase the cost.

The compacts may either be used as such or may be
sintered before addition to molten iron. In the unsintered
compacts the nickel coating on the particles serves to re-
strain the reaction of the magnesium with the molten
iron, while in the sintered compacts it reacts with the
magnesium during sintering to form intermetallic com-
pounds and solid solutions that react with only moderate
vigor with the molten iron. The intimate association of
the magnesium and the nickel of the coating provide very
favorable conditions for their interdiffusion and alloying

during sintering without loss of magnesium. The thickness of the coating is thus of importance both in green (unsintered) compacts and when they are sintered. In unsintered compacts a thicker coating delays contact between the magnesium and the molten iron to a greater extent than a thin coating, thereby damping down the subsequent reaction and giving a higher magnesium recovery. In making sintered compacts a certain amount of disruption of the coating to allow escape of molten metal is needed in order to sinter the particles together. Hence the nickel coating must neither be so thick that no disruption occurs nor be so thin that complete disruption occurs, thereby occasioning partial melting of the compacts and loss of material. The thickness of the coating depends both on the proportion of nickel to magnesium and on the size of the particles. For a given proportion of nickel and magnesium the thickness of the nickel coating decreases as the size of the base magnesium particle decreases. In practice magnesium particles smaller than 200 mesh BSS (0.075 mm.) cannot be used for coating, and for sizes down to this adequate coating thicknesses can be obtained when the coated particles contain from 50 to 90% of nickel.

We prefer to form the compacts wholly from nickel-coated magnesium powder, since this gives the highest degree of uniformity of composition. If desired, however, the nickel-coated magnesium powder may be admixed with powder of other constituents such as nickel, iron, silicon and copper commonly used as diluents in magnesium addition agents in order to moderate their reaction with molten iron. The use of any such diluent powder gives rise to risk of segregation in the compacts to the extent that the size and shape of the particles differ from those of the nickel-coated magnesium particles, but on the other hand a diluent powder may assist in moderating the reaction and thereby permit the nickel coating to be thinner than is otherwise required. In fact, with a large proportion of the diluent the weight of the nickel in the nickel-coated magnesium powder may be reduced, provided always that the magnesium particles are still completely coated, and indeed the proportion of nickel in the coated particles may then be as low as 15%. Thus, the compacts may contain substantial additional amounts of nickel powder, to bring the total nickel content of the compacts up to as much as 90% of the weight of the compacts, the maximum amount of added nickel being set by the need for an adequate coating of nickel on the magnesium particles while maintaining a sufficient magnesium content in the compact. The resulting compacts have the advantage of having no other constituents than nickel and magnesium. Iron, which is not as effective as nickel in moderating the violence of the reaction, may be present in amounts up to 30% of the weight of the compacts. Silicon, which has a moderating power between that of nickel and iron, and which is also useful as a graphitizing agent, may be present up to 70% of the weight of the compacts. Iron and silicon in the compacts may, if desired, be alloyed together as ferro-silicon powder.

Copper, the other common diluent metal, is an excellent moderator of the violence of the reaction, but in large amounts adversely affects the formation of spheroidal graphite in cast iron, and for this reason the proportion of any copper in the compacts should not exceed 30%.

The nickel coatings on the particles may be formed by any convenient method, but we prefer to deposit the nickel by the thermal decomposition of nickel carbonyl. In this way a continuous layer of nickel is formed over the particle surface and may be built up to any desired thickness, thus enabling the proportion of nickel to magnesium in the coated particles to be varied over a very wide range.

The green strength of the compacts is also affected by the particle size, decreasing as the particles become coarser, and for this reason in unsintered compacts the coated powder is preferably not larger than 72 mesh

BSS (0.2 mm.), and most advantageously not larger than 85 mesh (0.18 mm.). The strength of unsintered compacts may be increased, though at the expense of some loss in efficiency, by incorporating a small proportion of binder, e.g. a synthetic resin, either throughout the mix or as a surface layer. Alternatively, the compacts may be enclosed in bags or coverings, e.g. of polythene, to facilitate their handling. The highest efficiency is obtained when the coated powder does not contain any substantial proportion of particles smaller than 150 mesh (0.1 mm.).

When the compacts are sintered, coarser particles, e.g. from 10 to 60 mesh BSS (1.7 to 0.25 mm.), can be employed. However, sintering introduces a further processing operation with attendant increase in cost, and we prefer to employ the unsintered compacts.

The magnesium may be alloyed with small amounts of elements, e.g. up to 1% of silicon, added before it is coated to render it brittle and aid in the production of magnesium powder by pulverization of a cast ingot of magnesium. Care must however be taken to avoid any additions that have a deleterious effect on the formation of spheroidal graphite in cast iron.

The addition agents of the invention have many advantages compared with materials of similar composition prepared by melting, casting and crushing to size. Thus they can readily be made by standard powder-metallurgical procedures without appreciable loss of nickel or magnesium, whereas in preparing nickel-magnesium alloys by melting substantial losses are encountered. This is particularly advantageous in the case of addition agents of high magnesium content, e.g. about 30% or 40% to about 50%. For example, in melting a nickel-magnesium alloy containing 15% by weight of magnesium about 7% of the materials charged is lost as dross or otherwise during the melting process, and the losses in melting such alloys of higher magnesium content are still greater. In addition, when large pieces such as cakes, of such melted and cast material are crushed and sized to yield a marketable product further losses of material in the form of unusable fines are encountered. Furthermore, the melted alloys inevitably are somewhat dirty, i.e., contain dross and inclusions, whereas the compacts are clean. Unlike the broken pieces of the melted alloys, the compacts are readily made of regular and uniform shape and size, are easily packed, and have a reliably reproducible composition. Thus, they can be made to contain an accurately predetermined amount of magnesium, so that a given magnesium addition may readily be calculated by simply counting out the number of compacts to be added to a given metal.

When the addition agents of the invention are added to molten iron, e.g. for the production of spheroidal graphite cast iron, in a manner appropriate to their density, i.e. by plunging in the case of compacts having a magnesium content exceeding 15%, magnesium recoveries and efficiencies similar to or even better than those for melted alloys of the same composition are obtainable.

In order to obtain these advantages it is essential that the particles of magnesium powder used to form the compacts are coated with nickel. Unsintered addition bodies made by compacting mixtures of nickel and uncoated magnesium powders give lower magnesium recoveries when added to molten iron than unsintered compacts of similar composition made from nickel-coated magnesium powder, and attempts to sinter mixtures of nickel and magnesium powders lead to losses of magnesium owing to the low-melting point of magnesium and to the formation of a low melting-point eutectic.

In order to give those skilled in the art a better appreciation of the advantages of the invention, the following examples will now be given:

Example I

Magnesium powders of commercial purity having par-

ticle sizes of about 60 mesh BSS, in the range minus 85 to plus 120 mesh and in the range minus 100 to plus 150 mesh respectively, were coated with nickel by the thermal decomposition of nickel carbonyl to provide coated powders containing, by weight, about 60% nickel, the balance being magnesium. The initial powders were elongated in particle shape, some angular particles being present in the 60 mesh powder. The powders were briquetted at a pressure of about 30 long tons per square inch to produce strong cylindrical pellets having a diameter of about one inch and a height of about 0.75 inch. About 0.4% by weight of each of the resulting briquettes was introduced into separate portions of the same molten iron containing 3.81% carbon, 1.65% silicon, <2% manganese, 0.19% phosphorous and 0.01% sulfur while the molten iron was at a temperature of 1500° C. in each instance. Metal from each of the treated melts was cast and analyzed for magnesium. The results of these tests are summarized in the following Table I, which shows the progressive fall in recovery and efficiency with decreasing particle size. Each of the castings had a satisfactory spheroidal graphite structure.

TABLE I

Description of Pellets		Performance		
Magnesium Particle Size, mesh	Percent Nickel	Residual Magnesium Content, Percent	Average Magnesium Recovery, Percent	Average Alloy Efficiency, Percent
60-----	57.7	0.065 0.083	44.3	17.8
Minus 85, Plus 120----	58.2	0.058 0.061	41.6	16.6
Minus 100, Plus 150....	57.9	0.052 0.060	39.2	15.8

Example II

Magnesium powder containing about 0.5% silicon was coated with nickel by the thermal decomposition of nickel carbonyl to provide coated particles containing about 60% nickel, the balance being magnesium. The magnesium powder had a particle size of about 36 mesh and had a regular, angular shape. Portions of the coated powder were compacted at a pressure of about 30 long tons per square inch to provide cylindrical pellets having a diameter of about one inch and a height of about 0.75 inch. About 0.4% by weight of the as-pressed compacts were plunged into two other portions of the molten iron at 1500° C. as in Example I. Residual magnesium contents of 0.043% and 0.051%, representing an average magnesium recovery of about 33.7% and an average efficiency of about 13.5%, respectively, were obtained. The compacts obtained in this instance were noticeably more friable than those obtained using finer powders as set forth in Example I and the lower magnesium recovery obtained was attributed to this factor.

Example III

Atomised magnesium powder having a particle size range of 22 to 44 mesh BSS was coated with nickel by thermal decomposition of nickel carbonyl. The magnesium powder particles were rounded in shape, with a few re-entrants and the nickel coatings were from 20 to 30 microns thick and covered the whole surface fairly uniformly and filled the irregularities. The analysed nickel content of the powder was 58.8%. Portions of the coated powder were compacted under a pressure of 30 tons per square inch to form cylindrical pellets about one inch in diameter and about 0.75 inch high. These had fair green strength, but tended to crumble at the edges. Their strength was not significantly improved by heating at temperatures below 400° C., above which interdiffusion began to occur between the nickel and the magnesium as a preliminary to sintering.

On plunging 0.5% by weight of the as-pressed pellets into molten iron containing 3.68% carbon, 1.4% silicon,

0.2% manganese, 0.04% sulfur and 0.023% phosphorus, the balance being iron, at a temperature of 1500° C. a moderate reaction occurred and the iron when cast contained 0.066% magnesium and had a satisfactory spheroidal graphite structure.

Example IV

Pellets prepared as described in Example III were heated for 30 minutes at 650° C. in an atmosphere of dry hydrogen. Under these conditions the magnesium center of the particles just melted, and the nickel and magnesium reacted to form the intermetallic compound Mg₂Ni and the eutectic Mg/Mg₂Ni. Substantial amounts of the nickel coating remained unreacted and leakage of the molten metal through the nickel coating sintered the particles together and greatly increased the strength of the bodies.

On plunging 0.5% by weight of the sintered pellets into molten iron at 1500° C. the reaction was brisk but not so vigorous as to be hazardous. The iron when cast contained 0.042% magnesium and had a satisfactory spheroidal graphite structure.

Example V

Further compacted pellets prepared as described in Example III were heated for one hour in dry hydrogen at 725° C. i.e., below the temperature (760° C.) of peritectic formation of the intermetallic compound Mg₂Ni. Substantially all the nickel reacted with the magnesium to form Mg₂Ni and Mg/Mg₂Ni eutectic and the identity of the individual particles was almost lost in the sintered mass. Sintered pellets formed in this way, added in an amount of 0.5% to a further portion of the molten iron described in Example III at 1500° C. by plunging, reacted in a similar manner to the unsintered pellets to give an iron which, when cast, contained 0.059% magnesium and has a satisfactory spheroidal graphite structure. An attempt to sinter the pellets of Example III at a higher temperature, by heating for 15 minutes at 850° C., led to partial melting of the pellets and loss of material. The resulting bodies were not tested by addition to molten iron. For purposes of comparison, 0.5% of an experimental alloy made by a melting process and containing 60% nickel and 40% magnesium was also used to treat another portion of the same molten iron by plunging. The reaction on plunging was not over-vigorous, and the resultant cast iron contained about 0.05% magnesium and had a satisfactory spheroidal graphite structure.

Example VI

A mixture of 36.4 parts by weight of the nickel-coated magnesium powder used in Example III with 63.6 parts by weight of carbonyl nickel powder was compacted at 30 tons per square inch as in Example III to pellets having the composition 85% nickel-15% magnesium and the pellets were sintered by heating at 850° C. for 15 minutes. The resulting sintered bodies had a duplex structure consisting of nickel and the intermetallic compound MgNi₂. Despite the high temperature employed for sintering, the presence of the nickel powder substantially prevented loss of magnesium. When 1.0% of these bodies were added to molten iron at 1450° C. by tapping the iron on to the addition bodies, the reaction was not violent. Castings poured from the treated melt had a magnesium content of 0.073% and had a satisfactory spheroidal graphite structure. For purposes of comparison, a standard alloy of 85% nickel-15% magnesium made by adding magnesium to molten nickel was similarly added to another portion of the same iron melt. The vigor of the reaction was similar to that occurring with the sintered material, and the resulting iron contained about 0.052% magnesium, and had a satisfactory

spheroidal graphite structure. The results of Examples III to VI are summarised in the following Table II:

nesium, with the balance essentially nickel, said compact being made from an initial powder mix comprising mag-

TABLE II

Ex. No.	Addition Material	Addition Method	Residual Magnesium Content, percent	Magnesium Recovery, percent	Efficiency, percent
III-----	40% Mg, 60% Ni compacted-----	Plunged-----	0.066	48	19
IV-----	40% Mg, 60% Ni sintered 650° C-----	do-----	0.042	30	14
V-----	40% Mg, 60% Ni sintered 725° C-----	do-----	0.059	44	18
-----	40% Mg, 60% Ni melted-----	do-----	0.05	40	16
VI-----	15% Mg, 85% Ni sintered 850° C-----	Iron tapped on to addition material-----	0.073	69	10
-----	15% Mg, 85% Ni melted-----	do-----	0.052	55	8

It will be understood that the magnesium-containing addition agent according to the invention is also useful for treating molten metals with magnesium for purposes other than the production of ductile iron. Such purposes include the desulphurisation of cast iron and of steel.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. In the process for producing ductile iron wherein magnesium is employed to effect the occurrence of graphite in the spheroidal form, the improvement which comprises introducing magnesium into molten cast iron as a briquetted agent containing about 10% to about 50% magnesium, with the balance essentially nickel made from an initial powder mix comprising magnesium particles coated with nickel.

2. In the process for producing ductile iron wherein magnesium is employed to effect the occurrence of graphite in the spheroidal form, the improvement which comprises introducing magnesium into molten cast iron as a powder metallurgical compact containing about 10% to about 50% magnesium, with the balance essentially nickel, said compact being made from an initial powder mix comprising magnesium particles coated with nickel and having a particle size of not more than about 72 mesh BSS.

3. In the process for producing ductile iron wherein magnesium is employed to effect the occurrence of graphite in the spheroidal form, the improvement which comprises introducing magnesium into molten cast iron as a powder metallurgical compact containing about 40% mag-

nesium particles coated with nickel and having a particle size of not more than about 85 mesh BSS.

4. In the process for producing ductile iron wherein magnesium is employed to effect the occurrence of graphite in the spheroidal form, the improvement which comprises introducing magnesium into molten cast iron as a sintered powder metallurgical compact containing about 10% to about 50% magnesium, with the balance essentially nickel, said compact being made from an initial powder mix comprising magnesium particles coated with nickel and having a particle size from about 10 mesh to about 60 mesh BSS.

5. An addition agent for adding magnesium to molten metals consisting of compacts in which the magnesium is present as nickel-coated magnesium powder having a particle size not greater than 60 mesh BSS, and said magnesium amounts to from 10 to 50% by weight of the compacts, with the balance essentially nickel.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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John Oliver Hitchcock et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, line 10, "May 13, 1964," should read -- May 6, 1965, --. Column 1, line 43, "comomhly" should read -- commonly --. Column 7, line 50, "power" should read -- powder --.

Signed and sealed this 11th day of November 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents