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(71) Applicant *(for all designated States except US)*: **FOS INTERNATIONAL S.A.** [MH/MH]; Trust Comapny Complex, Ajeltake Road, Ajeltake Island, Majuro, Marshall Islands MH96960 (MH).

(72) Inventor; and

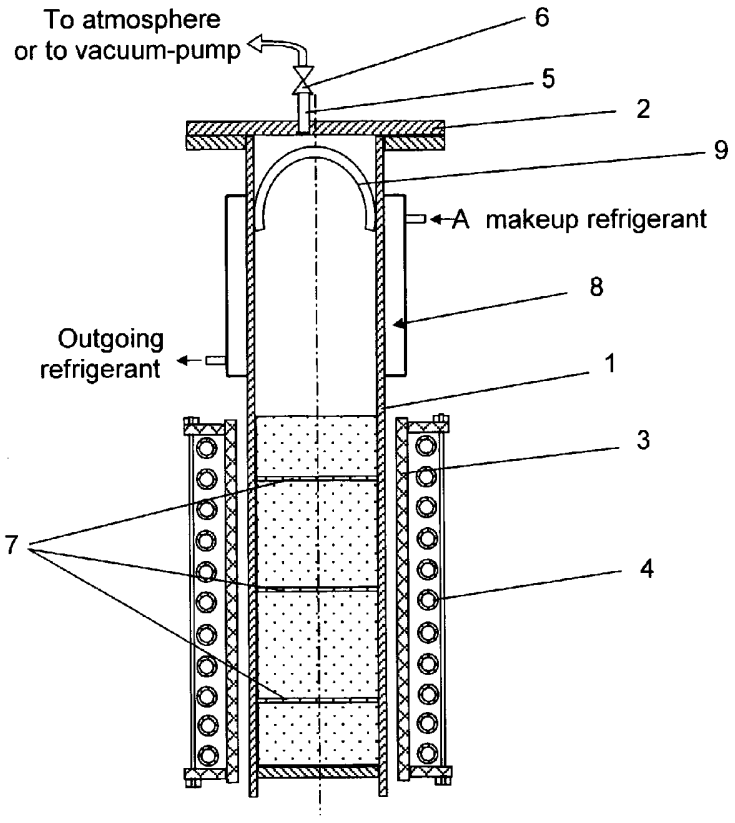
(75) Inventor/Applicant *(for US only)*: **PODOLTSEV, Oleksandr Dmitriyevich** [UA/UA]; ul. F. Pushinoy, 44/50-193, Kiev, 03179 (UA).

(74) Agent: **KUTSEVYCH, Valerii**; ul. Melnikova, 6-42, Kiev, 04050 (UA).

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(54) Title: METALLOTHERMIC PROCESS FOR MAGNESIUM PRODUCTION AND VACUUM-INDUCTION FURNACE THERETO



(57) Abstract: METALLOTHERMIC PROCESS FOR MAGNESIUM PRODUCTION is based on heating the batch mixture of calcined dolomite and ferrosilicon up to temperature of about 1200°C under residual pressure less than 670 Pa and condensing the magnesium vapor. To increase magnesium extraction, a batch mixture of fine-dispersed at least partially calcined dolomite consisted of particles of no more than 0.1 mm and low-silicon ferrosilicon is loaded into VACUUM-INDUCTION FURNACE having electroconductive crucible equipped with at least one additional electroconductive heater within heating area and cooling condenser on upper end. Each loaded batch mixture is calcined in good time at temperature of about 900°C under atmospheric pressure, then said furnace is closed and, after vacuuming, heated at temperature sufficient for beginning the metallothermic process, which is carried out on conditions that heat is supplied into volume of said charge.

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METALLOTHERMIC PROCESS FOR MAGNESIUM PRODUCTION AND VACUUM-INDUCTION FURNACE THERETO

Field of the Invention

This invention relates:

to metallothermic process for magnesium production from dispersed calcined dolomite raw using silicon-containing reducing agent, and

to vacuum-induction furnace for realization of this process.

Background Art

It is well known that industrial consumption of magnesium constantly increases, and substantial share of its global market is supplied by metallothermic processes. They do not generate by-products that are dangerous to industrial personnel and environment because the processes are carried out usually as solid-phase (**s**) reactions accompanied by sublimation of gaseous (***g***) magnesium according to canonical scheme

$$2(CaO \cdot MgO)\ (\mathbf{s}) + Si\ (\mathbf{s}) \rightarrow 2Mg\ (\mathbf{g})\uparrow + Ca_2SiO_4\ (\mathbf{s})\downarrow.$$

The calcined dolomite, which originally is a natural nearly equimolar mixture of calcium and magnesium carbonates, serves as a source of hard oxides of the said metals, and, as a rule, ferrosilicon, aluminum-silicon or their blends are used as a source of silicon. In this case, hard by-products containing iron and aluminum have chemical composition more complicated than that of calcium silicate.

Nevertheless, any metallothermic processing of the calcined dolomite has ecological advantages in comparison with electrochemical production of magnesium from practically waterless magnesium chloride.

An available to all Internet-review of «Metallothermic Reduction» (http:/www.magnesium.com/w3/data-bank) discloses that usual metallothermic process for magnesium production from dolomite raw includes following basic steps:

(1) preparation of a mixture of dispersed calcined dolomite and dispersed silicon-containing reducing agent (preferably ferrosilicon and, seldom, aluminum-silicon);

(2) pressing the mixture to obtain briquettes;

(3) loading said briquettes into reactor which comprises an *area for heating* the briquettes and *cooling area for magnesium vapor condensation*;

(4) heating said briquettes, reducing and sublimation of magnesium at temperature of about 1200°C and under residual pressure less than 670 Pa (preferably less than 400 Pa) with condensation of magnesium vapor in cooling area at temperature in the range of 400°C to 500°C;

(5) emptying and new-loading the reactor for repeating the metallothermic process (when it carries out in batch mode) or replenishment of heating area of the reactor by makeup mixture (when this reactor operates uninterruptedly).

The heating the mixture at temperature of about 1200°C is needed because the reaction of magnesium oxide reduction with silicon is highly endothermic, and vacuum is needed to lessen of the evaporation of magnesium from a nascent slag.

Nowadays three modifications of metallothermic processes for the industrial magnesium production, namely: Pidgeon Process, Bolzano Process, and Magnetherm Process are well known.

The above-mentioned step (1) is included into all these processes, and Pidgeon and Bolzano Processes have practically identical all steps of the magnesium production. Substantial differences between all said processes are related to reactors' design, conditions of mixture heating and conditions of magnesium evaporation, and evacuation of a slag arisen from remains of said mixture and by-products (this slag is solid free-flowing mass in Pidgeon Process and Bolzano Process, or fluid melt in Magnetherm Process).

Pidgeon Process was developed in the forties of XX century. It is carried out in such batch mode reactors as retorts which, after loading the briquettes immediately, must be closed and vacuumed. At the time of processing, at least two such retorts are placed vertically into heating furnace roof. This furnace is heated by liquid and/or gas hydrocarbon fuel. The heating area of each retort must be located within the furnace space, and the cooling area for magnesium vapor condensation must be located over the said furnace roof.

It is well known that even briquetted batch mixture has low thermal conductivity. Therefore, diameter of the retort opening is not more 300 mm usually, and is equal to 275 mm practically. It is well known also that even deep vacuum cannot provide magnesium vapor exhausting out of the lower layers of the batch mixture briquettes. Therefore, extreme height of the retort is usually not more 3,0 m, and their load doesn't reach the half volume. Unfortunately, either of these limitations is insufficient for uniform heating the full mass of the batch mixture with an *external* heat source. Correspondingly, 24 hours' magnesium yield to one retort averages about 70 kg. Moreover, mixture must be primarily dried and prepared on base of such dolomite that contains no less than 99.5% calcium and magnesium carbonates and such high-silica ferrosilicon that contains no less than 65%, preferably to 90%, silicon and is taken in amount that exceeds somewhat the stoichiometric relationships. Only fulfillment all these requirements allows to extract no less than 90% magnesium that was contained initially in batch mixture and to provide for its purity no less than 99.95%.

More efficient Bolzano Process provides an *internal* batch mixture heating at temperature about 1200°C and under residual pressure less than 400 Pa.

Compact vacuum bell-type furnaces are used thereto. Each such furnace comprises steel housing that includes a cylindrical heating lower section and a

removable cylindrical-spheroidal cooling upper section. The lower housing section is lined on the inside by refractory brick and equipped with a support for mixture briquettes and such contactors for connection to a current source that being adjacent tightly to ends of a set of said briquettes when the furnace operates. The upper housing section is equipped with a water jacket and has at least one (as a rule central) opening for connection of the furnace space to a vacuum source and to atmosphere.

However, magnesium vapor permeability of the briquettes set decreases when height and consistence of said set increase. Further, current density and, correspondingly, heat development do not be equal in different cross-sections of said set in principle. Therefore, magnesium wastes with slag is increased in accordance with enhancement of height and volume temperature inhomogeneity of said set. Even if ferrosilicon contains more than 78% silicon by weight, no more than 81% silicon may be used for magnesium reduction. These silicon wastes with slag raise essentially the price of base product.

A first common disadvantage of Pidgeon and Bolzano Processes is impossibility of utilization of fine-dispersed calcined dolomite wastes that arise in tube kilns in the course of fluxing agents' production for ferrous metallurgy or intermediate products for refractories. Such wastes may be transforming, under the action of atmospheric moisture, at least partially in chemically active magnesium and calcium hydroxides that are dangerous to environment and unsuitable for direct incorporation to briquetted mixture. Thus, their cumulation at dumping places is a "headache spring" for managers of respective plants and for ecological inspection for a long time.

One more common disadvantage of the Pidgeon and Bolzano Processes is demand of conditioned ferrosilicon contained no less than 65% silicon.

These disadvantages cannot be eliminated by high capacity Magnetherm Process that is the most similar to proposed further process in subject matter. It is known since 1963 and takes place as interaction between the solid (***s***), liquid (***l***) and gaseous (***g***) phases according to the scheme:

$$(CaO \cdot MgO)\ (\boldsymbol{s}) + Al_2O_3\ (\boldsymbol{s}) + (Fe)Si\ (\boldsymbol{s}) \rightarrow Mg\ (\boldsymbol{g})\uparrow + (CaO \cdot SiO_2 \cdot nAl_2O_3)\ (\boldsymbol{l}).$$

Magnetherm Process includes:

(1) preparation of a mixture of dispersed calcined dolomite raw, dispersed silicon-containing reducing agent, and aluminum oxide (that is taken, especially, as alumina);

(2) loading a batch mixture into reactor having an area for electrical heating the mixture and nascent slag and cooling area for magnesium vapor condensation;

(3) vacuuming the reactor at residual pressure in the range of 400 Pa to 670 Pa, electrical heating the mixture within the reactor at temperature no more than 1200°C sufficient for reduction and sublimation of magnesium, and nascent slag melting at temperature in the range of 1550 to 1600°C;

(4) precipitation of magnesium vapor within the cooling area (where temperature is usually no more than 500°C);

(5) removal of the slag from the reactor and repeating the production cycle starting with step (*1*) when process carrying out in batch mode, or replenishment of the heating area with make-up mixture and at least repeatable slag discharge when process carrying out continuously.

Under steady-state conditions, redox reaction is occurred in solid phase as results of impingement of the calcined dolomite, ferrosilicon and alumina particles on surface of the slag melt. This allows to use such mixture that consists of rather coarse all ingredients' particles with diameter in the range of 3 to 30 mm, and ferrosilicon contained less than 65% of silicon.

However, it was determined experimentally that the ferrosilicon particles, in which silicon concentration is decreased to 20%, goes down in slag melt, and spontaneous breaking the magnesium production is possible. Therefore, the mixture used in Magnetherm Process is usually delivered into reactor in parts. But even such reactor feed, observable amount of magnesium oxide and silicon give no chemical interaction and go down in slag. Therefore, no less than 10% of magnesium amount initially contained in calcined dolomite goes off with slag.

A reactor for Magnetherm Process has two parts.

A first axisymmetric heated part comprises:

a heat-resistant housing that is lined near-bottom by refractory body,

a first practically vertical copper nonconsumable electrode rigidly fixed into the housing roof in such a way that its geometrical axis is practically coincident with axis of symmetry of said first part;

a graphite lining supported by said refractory body and served as a second practically nonconsumable electrode;

a bypass channel for passing the magnesium vapor from underroof space of the said first part into second (condensation) part of the reactor;

a tap hole for slag removal from the graphite lining.

Second (not necessarily axisymmetric) part has a sectional housing. Upper cone-shaped cooling section of this housing serves as a condenser of the magnesium vapor. This section is connected with said first part by above-mentioned bypass channel and equipped with at least one vertical nipple for connection to a vacuum source and to atmosphere. Lower section of this housing serves as a downtank of base product.

However, use of the described reactors for high-purity magnesium production causes unreasonable capital and operating costs. Especially, each of the known reactors cannot be supplied with easily accessible low-grade row materials such as:

above-mentioned fine-dispersed calcined dolomite wastes (because they must be dried thoroughly and at least pelleted before magnesium reduction), and

reducing agents contained less than 50% of silicon (because their reduction potential is too small for Magnetherm Process).

It is possible (but taking into consideration the prior art, no more than possible) to use the said low-grade row materials for metallothermic magnesium production because vacuum-induction furnaces having the crucibles produced from electroconductive materials such as heat-resistant (not necessarily ferromagnetic) steels are suitable for this purpose in principle.

Especially, it is known induction furnace for magnesium melting (Брокмайер К. Индукционные плавильные печи. – Перевод с немецкого под редакцией М.А. Шевцова and М.Я. Столова. – М.: «Энергия», 1972, с.92-95, рис. 3-31; Brokmayer K. Induction melting furnaces. – Translated from German under the editorship of M.A. Shevtsov and M.Ya. Stolov. – Moscow: "Energia" Publishing House, 1972, pp. 92-95, Fig. 3-31). This furnace has a steel crucible and surrounding a heat-insulating mantle and an inductor (e.g. equipped with three-phase winding that may be used for supply by current of commercial frequency).

This furnace cannot be used for metallothermic magnesium production because it has no vacuuming and magnesium vapor precipitation means.

DE 4209964 closes such vacuum-induction furnace that is the most similar to subject matter of the furnace proposed below. Known furnace comprises –

an electroconductive (e.g, steel) crucible intended for placing and processing of the batch mixture,

a removable cover for hermetic seal of the crucible,

a heat-insulating mantle and an inductor, which are surrounded at least the lower part of the crucible, and

means for alternate connection of the furnace space to a vacuum source or to atmosphere,

However, this furnace (if even would be equipped with metal vapor trap) may be suitable theoretically only for metallothermic extraction of magnesium from mixture of partially calcined dispersed damp dolomite and dispersed silicon-containing reducing agent. The point is that such mixture has no appreciable ferromagnetic properties, and practically loses electroconductivity after pre-drying. Thus, each batch mixture may be heated only by emission from the crucible wall to an adjacent to this wall low heat-conducting blanket composed of the powder mixture. It is obvious that crucible heating efficiency decreases sharply when temperature exceeds the Curie point. Evidently this, is why up to the present day the vacuum-induction furnaces are not in use for metallothermic magnesium production.

Brief Description of the Invention

The invention is based on the problem, by way of improvement of mixture processing conditions, to create such metallothermic process and such vacuum-induction furnace, which would increase magnesium extraction from a low-grade calcined dolomite raw and a low-silicon ferrosilicon.

This problem is solved in that metallothermic process for magnesium production includes the following steps:

preparation of mixture of dispersed at least partially calcined dolomite raw and dispersed silicon-containing reducing agent,

loading the batch mixture into a reactor that has an area for heating the batch mixture and a cooling area for magnesium vapor condensation,

vacuuming the reactor at residual pressure no more than 670 Pa and heating the batch mixture within the reactor up to temperature no more than 1200°C sufficient for the metallothermic process of magnesium reduction and sublimation,

precipitation of magnesium vapor in said cooling area,

depressurizing the reactor, evacuation of the base product from the cooling area and the slag from the heating area to preparation for repeating the production cycle,

and, *according to the invention*, the process further provides

use, as reactor, a vacuum induction furnace that has an electroconductive crucible equipped, within the located near the bottom heating area, with at least one additional electroconductive heating element, and, on the upper part, with a cooler on the outside and with a magnesium vapor trap inside,

preparation of the mixture from fine-dispersed dolomite raw that mainly contains particles with diameter less than 0.1 mm, and reducing agent that contains no less than 45% silicon by weight,

calcination of each batch mixture, after its loading into said furnace, in good time in contact with atmosphere at temperature lower starting metallothermic process temperature during the time enough for practically full dewatering and degassing of said batch mixture,

closing the crucible of said furnace after completion of said preliminary calcination of said batch mixture, and then vacuuming the furnace space at above-mentioned residual pressure and inductive heating of said dried and degasified mixture at temperature sufficient for start of the metallothermic process,

stoppage of the vacuuming after start of the metallothermic process, and continuation of the heating the batch mixture up to temperature no more than 1200°C under heat supply deep into free-flowing mass of batch mixture and nascent slag until termination of magnesium sublimation and its vapor precipitation.

Synchronous heating of the mixture based on fine-dispersed dolomite raw

material, from crucible wall and from at least one additional electroconductive element within furnace space, allows:

firstly, to reduce magnesium efficiently even if ferrosilicon contains about 45% of silicon, and

secondly, to decrease substantially magnesium wastes with slag (up to 4.5% of its basic amount).

First and second additional features are consisted, correspondingly, in that

partially calcined dolomite powder that is waste of industrial dolomite calcination as fine-dispersed dolomite raw is used, and

waste of ferrosilicon production that consists of no less 45% of silicon by weight as reducing agent is used.

These raw materials are available at knockdown prices and their processing allows substantially decrease pollution of the environment by ferrous metallurgy and refractory works that are used dolomite as auxiliary and/or main raw material, respectively.

Third additional feature consists in that each loaded into furnace batch mixture is preliminary calcined in contact with atmosphere at temperature in the range of 885°C to 920°C. This temperature interval is the most useful for practically completed dewatering the raw material, destroying the magnesium and calcium hydroxides and carbonates of these metals residue with evacuation of the nascent water vapor and carbon dioxide into atmosphere during usually no more one hour.

The problem is also solved in that in the vacuum-induction furnace comprising:

a produced from electroconductive material crucible intended for placing and processing of the batch mixture,

a removable cover for hermetic seal of the crucible,

a heat-insulating mantle and an inductor, which are surrounded the lower part of the crucible, and

means for alternate connection the furnace space to a vacuum source or atmosphere,

according to the invention

the crucible is equipped, within the heating area that meant for placing and processing the metallurgical raw mixture, with at least one additional electroconductive heating element, and, on the upper part, with a cooler on the outside and with a metal vapor trap inside.

These improvements transform the vacuum-induction furnace to high-efficient reactor meant, in particular, for metallothermic magnesium production from arbitrary low-grade at least partially calcined dolomite raw and low-silicon ferrosilicon.

First additional feature consists in that said additional electroconductive heating

elements are selected from group consisting of at least one lateral rod, at least one membrane having at least one through-hole, at least one plate, a spiral insert which has a lead angle that exceeds the angle of free-flowing raw and/or slag friction and is formed as unbroken vane or consequently arranged separate vanes, and an arbitrary set of these component parts. This list includes the most preferable shapes of the additional electroconductive heating elements that can provide for temperature homogenizing within batch mixture and nascent slag mass.

Second additional feature consists in that said trap is formed as plug-in shell. This feature allows saving time at re-loading of the vacuum-induction furnace after completion of each regular production cycle.

It is clear for the person skilled in art that neither selection of each specific mode of carrying out of the invention by way of arbitrary combination of the basic inventive idea with said additional features and described below preferable examples of carrying out of the invention are not confined the measure of rights based on claims.

Brief Description of the Drawings

The invention will now be explained by detailed description of a vacuum-induction furnace and metallothermic process for magnesium production with reference to the accompanying drawings wherein:

Fig.1 shows schematic longitudinal section of a vacuum-induction furnace equipped with an inductor having a single-phase winding;

Fig.2 shows schematic longitudinal section of a vacuum-induction furnace equipped with an inductor having three-phase winding;

Fig.3 shows cross-section of a crucible at rod additional electroconductive heating elements level;

Fig.4 shows cross-section of a crucible at additional electroconductive heating element level (this element is shaped as membrane having a central through-hole);

Fig.5 shows cross-section of a crucible at additional electroconductive heating element level (this element is shaped as a membrane having several through-holes);

Fig.6 shows schematic longitudinal section of the crucible that equipped with such additional electroconductive heating elements, which are shaped as stepwise mounted plates.

Best Mode Carrying Out the Invention

A simplest vacuum-induction furnace according to the invention (see Fig.1) has:

a produced from electroconductive (usually ferromagnetic) material preferably plug-in crucible 1 for placing and processing of a batch mixture,

a removable cover 2 for hermetic seal of the crucible 1,

a heat-insulating mantle 3 and a having single-phase winding inductor 4, which are surrounded consequently the lower part of the crucible 1,

means for alternate connection the furnace space to a vacuum source or atmosphere, namely: at least one nipple 5 that is connected, as a rule, to the cover 2, and at least one locking and regulating element (e.g., a three-way tap or valve) 6,

at least one additional electroconductive (preferably ferromagnetic) heating element 7 that is rigidly connected inside to the wall of lower part of the crucible 1,

a cooler 8 that, at least when operates, surrounded tightly the upper part of the crucible 1 from the outside and formed, as a rule, as a flow-through shell-and-tube heat exchanger (in particular, a water-jacket), and

a metal vapor trap that is formed usually as plug-in shell 9 and placed within the crucible 1 at working area of the cooler 8 when it operates.

Shapes of cross-section of the crucible 1 may be very various. Preferably, if the crucible 1 is axisymmetric but most preferably, if it would be produced as such piece of an annular cylindrical pipe that equipped with a hermetically welded bottom from below and a flange for fastening the cover 2 at upper end.

The inductor 4 having single-phase winding may be connected to an arbitrary alternating (commercial or high frequency) current source. Nevertheless, it is advisable that the furnaces, equipped with such inductors 4, are taken in a divisible by three numbers and combined as tri-furnaces' units. Then the each single-phase winding of each this unit may be connected to a single phase of three-phase alternating current industrial network at a frequency of 50 or 60 hertz.

Fig.2 shows vacuum-induction furnace equipped with such inductor 4, the three-phase winding of which meant for connecting to the above-mentioned three-phase industrial network.

The heat-insulating mantle 3 is made of a material permeable to electromagnetic field and is fixed between the outside crucible 1 wall and the inductor 4 winding(s).

The additional electroconductive heating elements 7 may be various in geometric form and dimensions and may be selected from group consisting of:

at least one rod but preferably as a grate composed from transverse or crossing and tight interlocked rods which, in aggregate, are comprise the closed circuit for circular movement of induced eddy currents (see. Fig.3 wherein the curved arrow indicates one of two possibles closed current path),

at least one membrane having at least one preferably central through-hole (Fig.4) or several through-holes (Fig.5) for batch mixture loading and free-flowing slag removal (these membrane, irrespective of shape, number and arrangement of the through-holes, must be providing the such closed circuits for circular movement of induced eddy currents which are indicated by the curved arrows),

at least one plate but preferably a set arranged stepwise entire or perforated plates (see Fig.6),

a spiral insert not showed apart, which has always a lead angle that exceeds the angle of free-flowing raw and/or slag friction and may be formed as unbroken (and perforated usually) vane or preferably as consequently arranged separate (entire or perforated) vanes, and

an arbitrary set of these component parts.

The described above furnace equipped with the additional electroconductive heating elements 7, irrespective of a concrete construction, may be used efficiently as a reactor for metallothermic metal production using free-flowing mixture of oxide of desired metal and suitable reducing agent.

The said furnace was designed originally for metallothermic magnesium production. Therefore, its operation is described below by the example of this process.

Metallothermic process for magnesium production using the described furnace includes the following steps:

(1) preparation of a mixture:

a) of a fine-dispersed at least partially calcined dolomite raw material that mainly contains particles with diameter less than 0.1 mm (i.e. preferably such usually dumped wastes of industrial dolomite calcination that arise, as a hygroscopic powder, within tube kilns at temperature about 1100°C in amount up to 30% of basic dolomite weight), and

b) of a dispersed ferrosilicon waste contained at least 45% of silicon by weight;

(2) loading a batch mixture into the lower part of the empty crucible 1 up to level no higher than the upper end of the inductor 4 winding;

(3) preliminary calcination of the loaded batch mixture, when the cover 2 of the crucible 1 is open, at temperature lower starting metallothermic process temperature (preferably in the range of 885°C to 920°C) during the time enough for practically full dewatering and degassing of said batch mixture as a result of volatilization of the water vapor and carbon dioxide into atmosphere;

(4) placing into upper part of the crucible 1 of the plug-in shell 9 and closing the cover 2;

(5) vacuuming the crucible 1 through the nipple 5 and the locking and regulating element 6 connected to not shown apart vacuum-pump at residual pressure no more than 670 Pa (preferably less than 400 Pa), and heating of all batch mixture by heat transfer from the wall inside of the crucible 1 and from the surface of the additional electroconductive heating elements 7 up to temperature no more than 1200°C (preferably about of 1150 to 1170°C) sufficient for start of the metallothermic process;

(6) stoppage of the vacuuming after of the metallothermic process start (by switching the locking and regulating element 6 in «closed» position), engaging the cooler 8 and prolongation of heating under heat supply deep into free-flowing mass,

preferably by means of heating elements 7, for maintenance of the temperature of the batch mixture and nascent slag of about 1200°C (desirably in the range of 1150°C to 1170°C) until termination of the magnesium sublimation and its vapor precipitation on the trap (i.e. plug-in shell) 9;

(7) tail-end steps, namely:

(7a) switching off the feed of the inductor 4 for stopping the slag heating that is originated as a result of the chemical reactions between batch mixture ingredients and magnesium sublimation,

(7b) depressurizing the crucible 1 (by switching the locking and regulating element 6 to atmosphere),

(7c) pulling-off the cover 2 when pressure in the crucible 1 puts on a par with a barometric pressure current value,

(7d) removal of the plug-in shell 9, which contains a bootleg (in this case, magnesium), from the crucible 1,

(7e) removal of the slag from the crucible 1; and

repeating the production cycle as described above.

Above-mentioned wastes of dolomite calcination, which can be used in proposed process as preferable batch mixture ingredient, have usually, in anticipation of fully dry substance, the following averaged composition (see Table 1):

Table 1

AVERAGED COMPOSITION OF THE USUAL CALCINED DOLOMITE WASTES

Ingredients	Mean concentration, % by weight
Magnesium oxide	32.05 (including Mg 19.25)
Calcium oxide	40.56
Silicon dioxide	13.20
Aluminum oxide	6.13
Trivalent iron oxide (Fe_2O_3)	2.84
Impurities	the rest

Data indicated in column 2 were determined as a result of analysis of calcined to the constant mass samples of the dolomite wastes that were obtained in tube kilns of the Joint Stock Company "Severstal" (Cherepovets, Russia) and retained at dumping place together with other wastes of fluxing agents' production.

Calcination of said samples is needed because a base of the dolomite calcination wastes is the hygroscopic magnesium and calcium oxides. Therefore, these wastes are contained always a moisture (including water that is bonded chemically in $Mg(OH)_2$ and $Ca(OH)_2$ molecules, and free-water impurities). Respectively, the total moisture values of the calcined dolomite wastes must be taken into account in the course of usual technical chemical calculations of supply rates of the magnesium oxide containing raw and the silicon-containing raw before preparation of prescribed batch mixture portions.

It is preferable to use (and were used) low-silicon wastes of blast-furnace production of ferrosilicon as silicon-containing reducing agent (see Table 2). These wastes are retained today at dumping places of ferrosilicon works in abundance.

Table 2

AVERAGED COMPOSITION OF THE FERROSILICON WASTES BEFORE SILICON ENRICHMENT

Ingredients	Concentration, % by weight
Silicon (with a touch of silicon dioxide)	41.06
Aluminum oxide	19.83
Magnesium oxide	3.52
Iron	the rest

Enrichment of said wastes up to needed no less than 45% silicon concentration may be carried out with any suitable means.

More than 100 pilot experiments with metallothermic magnesium production using above-mentioned raw and experimental vacuum-induction furnace were carried out for evaluation of practicability of the invention.

Cylindrical crucible 1 of said experimental furnace was produced from heat-resistant chromium-nickel steel. It had:

the general height of 1650 mm;

the internal diameter of 200 mm;

the wall thickness of 36.5 mm;

the bottom's thickness of 36.5 mm and distance of 157 mm between the lower side of the bottom and the support of the crucible;

the total heating area height of 685 mm;

the transition (not included into heat-insulated jacket) area of 175 mm in height;

the cooling (equipped with water-jacket 8 as cooler) area of 410 mm in height.

The inductor 4 was equipped with single-phase winding and designed for peak active power consumption at 50 kWh. Each additional heating element 7 was formed as welded grate (lattice) composed of the ferromagnetic heat-resistant steel rods. Three said grates were welded to crucible 1 wall within the heating area for the distances of 190 mm, 390 mm and 590 mm from the lower side of the crucible 1 bottom.

At the starting time of warming-up of the crucible 1, these latticed elements 7 were served mainly as heat-conductors for heat supply into damp mixture that contains residual impurities of magnesium and calcium carbonates. After transition of the crucible 1 material through Curie point, the latticed elements 7 were transformed to basic heat source for sufficient homogenous batch mixture heating (because heating said elements 7 by induced eddy currents is continued). Finally, said elements 7 are able, during metallothermic process, to prevent the magnetism stratification of the free-flowing mass of the batch mixture residue and the nascent slag under the influence of inductor's 4 magnetic field. Thus, conditions of chemical interaction of the non-

ferromagnetic magnesium oxide particles and ferromagnetic ferrosilicon particles were ameliorated substantially so as to use the reduction potential of the low-silicon ferrosilicon.

The mixture proportion was determined according to data of quantitative raw-compositional analysis taking into account the ratio (CaOMgO):(FeSi)=5:1. Fine-dispersed mixture ingredients were mixed by rotary mixing machine to practically homogeneous mass, then obtained mixture was divided into equal parts (up about 100 kg by weight) for sequential loading into crucible 1.

Average duration of the single processing steps were as follows:

preliminary calcination of each loaded batch mixture (at temperature of about 900°C when the cover 2 is open) – up to 50 minutes,

vacuuming and heating at starting metallothermic process temperature (more than 1150°C but no more than 1200°C when the cover 2 is closed) – up to 35 minutes,

metallothermic process following the magnesium sublimation and its vapor precipitation on plug-in shell 9 when the cover 2 is closed – of 30 to 40 minutes.

Purity of precipitated magnesium, as a basic product, was 99.957% by weight on the average. As impurities were detected (% by weight): zinc (up to 0.007), copper (up to 0.005), iron (up to 0.011), and aluminium (up to 0.020).

As basic components of the slag were detected (% by weight): caustic lime (up to 52.5), silicon dioxide (up to 27.1), trivalent iron oxide (up to 8.0), and aluminium oxide (up to 8.0). Data of chemical analysis of the raw materials and of the slag comparison was revealed that reactive silicon was lacking practically in all slag samples, while magnesium residual in slag was no more than 6.0% and, on average, about 4.5% from initial value.

Industrial Applicability

The combined external and internal heating of each batch mixture within the vacuum-induction furnace according to the invention allows to extract the magnesium from fine-dispersed dolomite calcination wastes using low-silicon wastes of ferrosilicon production, and hence, to ameliorate environment. This source of raw materials for magnesium production according to invention will be existing so long as will be existing ferrous metallurgy and refractories production based on dolomite.

CLAIMS

1. Metallothermic process for magnesium production, the process includes the following steps:

preparation of mixture of dispersed at least partially calcined dolomite raw material and dispersed silicon-containing reducing agent,

loading the batch mixture into a reactor that has an area for heating the batch mixture and a cooling area for magnesium vapor condensation,

vacuuming the reactor at residual pressure no more than 670 Pa and heating the batch mixture within the reactor up to temperature no more than 1200°C sufficient for the metallothermic process of magnesium reduction and sublimation,

precipitation of magnesium vapor in said cooling area,

depressurizing the reactor, evacuation of base product from the cooling area and slag from the heating area to preparation for repeating the production cycle,

characterized in that

as reactor is used a vacuum induction furnace that has an electroconductive crucible equipped, within the located near the bottom heating area, with at least one additional electroconductive heating element, and, on the upper part, with a cooler on the outside and with a magnesium vapor trap inside,

the mixture is prepared by mixing of a fine-dispersed dolomite raw material that mainly contains particles with diameter less than 0.1 mm, and reducing agent that contains no less than 45% silicon by weight,

each batch mixture, after loading into said furnace, is calcined in good time in contact with atmosphere at temperature lower start metallothermic process temperature during the time enough for practically full dewatering and degassing of said batch mixture,

after completion of said preliminary calcination of the said batch mixture, the crucible of said furnace must be covered, the furnace space must be vacuumed at above-mentioned residual pressure, and said dried and degasified mixture must be inductively heated at temperature sufficient for start of the metallothermic process,

after start of the metallothermic process, vacuuming must be stopped but heating the batch mixture at temperature no more than 1200°C must be prolongate under heat supply deep into free-flowing mass of batch mixture and nascent slag until termination of magnesium sublimation and its vapor precipitation.

2. Process according to claim 1 *characterized* in that the partially calcined dolomites powder that is waste of industrial dolomite calcination as fine-dispersed dolomite raw material is used.

3. Process according to claim 1 or claim 2 *characterized* in that the ferrosilicon production wastes as reducing agent contained no less than 45% silicon by

weight are used.

4. Process according to claim 2 or claim 3 *characterized* in that each loaded into furnace batch mixture is preliminary calcined in contact with atmosphere at temperature in the range of 885°C to 920°C.

5. Vacuum-induction furnace, the furnace comprising:

a produced from electroconductive material crucible intended for placing and processing of the batch mixture,

a removable cover for hermetic seal of the crucible,

a heat-insulating mantle, and an inductor, which are surrounded the lower part of the crucible, and

means for alternate connection the furnace space to a vacuum source or atmosphere,

characterized in that

the crucible is equipped, within the heating area that meant for placing and processing the metallurgical raw mixture, with at least one additional electroconductive heating element, and, on the upper part, with a cooler on the outside and with a metal vapor trap inside.

6. Furnace according to claim 5 *characterized* in that said additional electroconductive heating elements are selected from group consisting of –

at least one lateral rod,

at least one membrane having at least one through-hole,

at least one plate,

a spiral insert which has a lead angle that exceeds the angle of free-flowing raw and/or slag friction and is formed as unbroken vane or consequently arranged separate vanes, and

an arbitrary set of these component parts.

7. Furnace according to claim 5 or claim 6 *characterized* in that said trap is formed as plug-in shell.

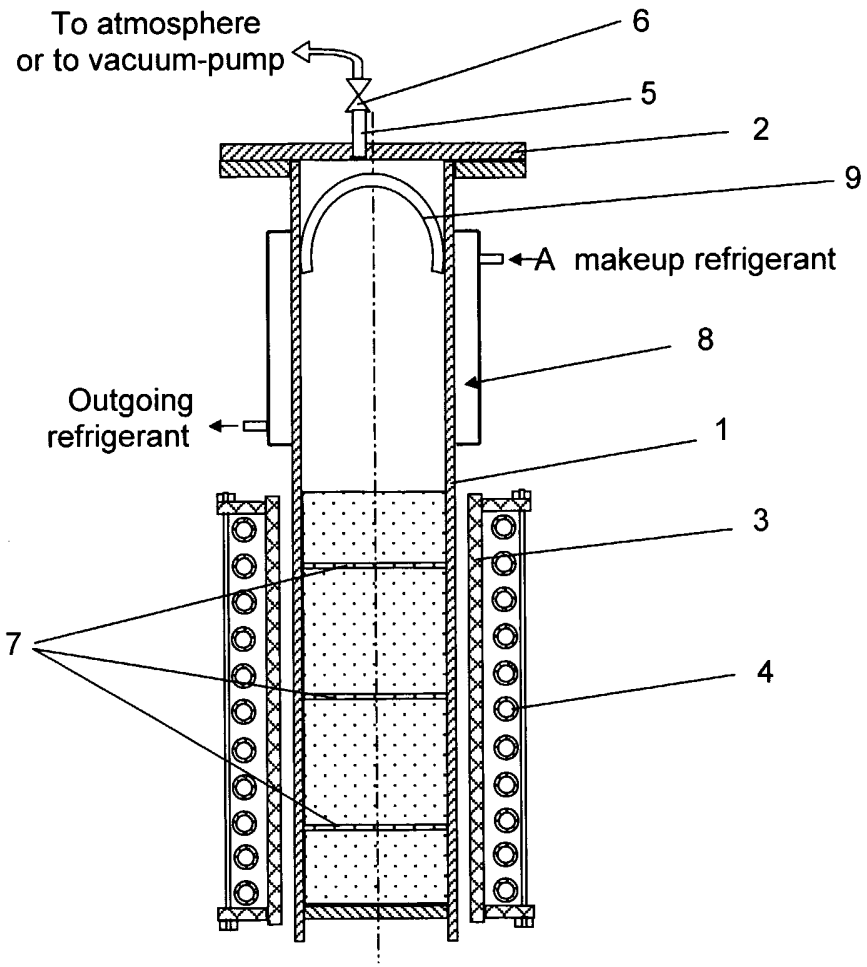

To atmosphere
or to vacuum-pump
6
5
2
9
A makeup refrigerant
8
Outgoing
refrigerant
1
3
7
4

Fig.1

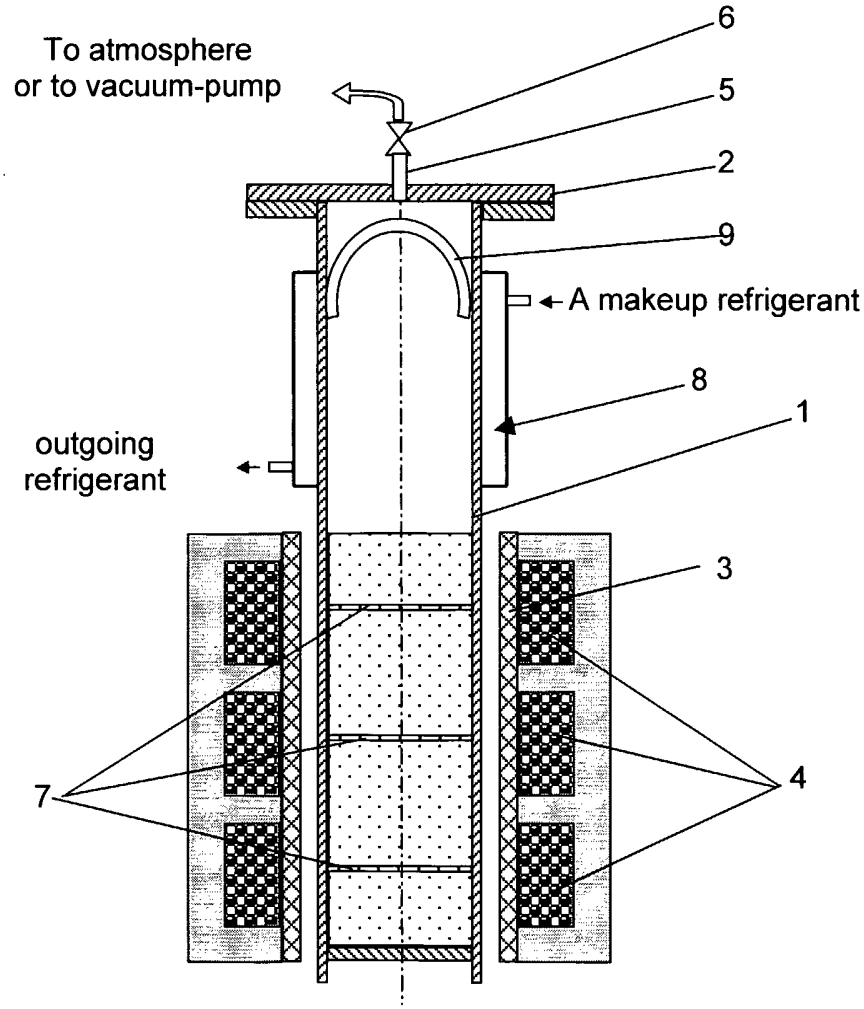

To atmosphere
or to vacuum-pump
6
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A makeup refrigerant
8
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outgoing
refrigerant
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7
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Fig.2

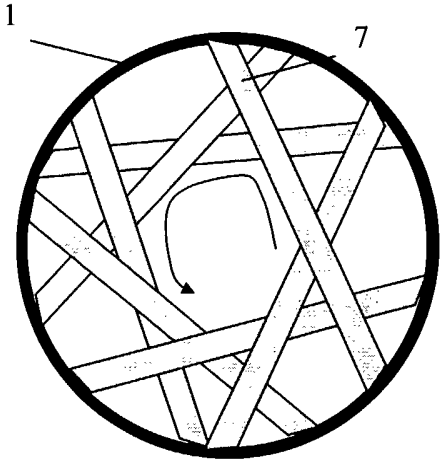


Fig.3

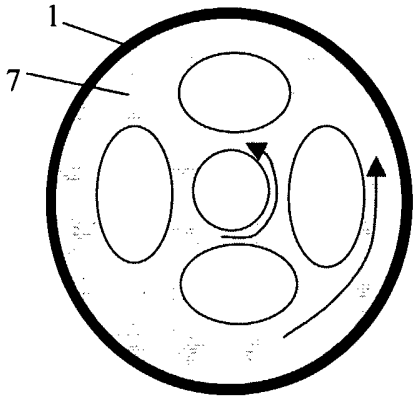


Fig.5

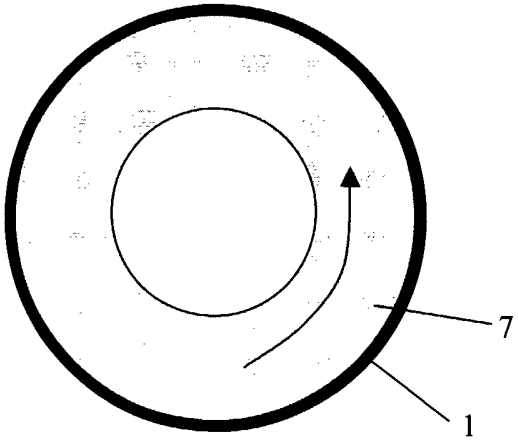


Fig.4

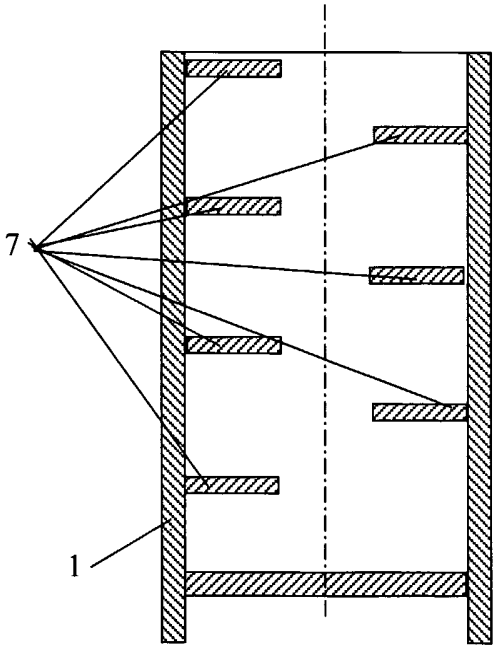


Fig.6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JA2004/000047

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B26/22 C22B5/16 F27B14/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B F27B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 165 742 A (LAWRENCE TURNER WILLIAM ET AL) 11 July 1939 (1939-07-11) page 2, lines 11-70; example II	1-7
A	CA 2 104 983 A (BILLY JEAN MARC ; LALANCETTE JEAN MARC (CA)) 28 February 1995 (1995-02-28) page 12, lines 10-19; page 13, lines 6-8	1-7
A	US 5 698 158 A (MARX DANIEL R ET AL) 16 December 1997 (1997-12-16) abstract; figures	5-7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 December 2004	13/01/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bjoerk, P

INTERNATIONAL SEARCH REPORT

nformation on patent family members

Ir ional Application No
PCT/UA2004/000047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2165742 A	11-07-1939	NONE	
CA 2104983 A	28-02-1995	CA 2104983 A1	28-02-1995
US 5698158 A	16-12-1997	US 5582630 A	10-12-1996
		AU 4147996 A	11-09-1996
		CH 689865 A5	31-12-1999
		DE 19581926 T0	12-02-1998
		JP 11502565 T	02-03-1999
		LU 90125 A1	13-11-1997
		WO 9626297 A1	29-08-1996