

[54] PROCESS FOR PRODUCTION OF MAGNESIUM 3,441,402 4/1969 Magee et al. 75/67 R
3,837,843 9/1974 Pons et al. 75/67 R

[75] Inventors: Tomoo Matsushima; Tsutou Odajima, both of Yokohama, Japan

Primary Examiner—C. Lovell
Assistant Examiner—M. J. Andrews
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[73] Assignee: Showa Denko Kabushiki Kaisha, Tokyo, Japan

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[57] ABSTRACT

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[51] Int. Cl.²..... C22B 45/00

[58] Field of Search..... 75/67 R, 67 A, 10 A, 3, 75/24

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Magnesium is produced from a mixture of magnesium oxide and calcium oxide by blending the mixture with silicon or ferro-silicon and shaping the blend in the form of briquets, heating the briquets in an inert atmosphere under temperature and pressure conditions capable of substantially inhibiting formation of magnesium vapor, said temperature being not lower than the melting point of calcium-silicon alloy, and thereby producing calcium-silicon alloy within said briquets and subsequently heating the briquets for thereby reducing magnesium oxide.

7 Claims, 7 Drawing Figures

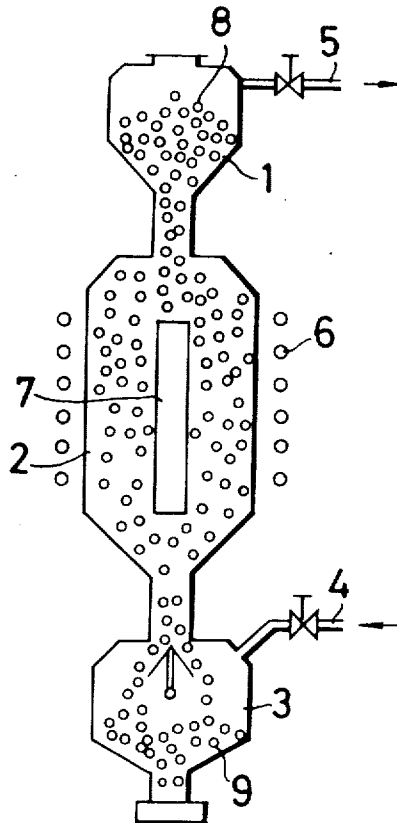


Fig. 1

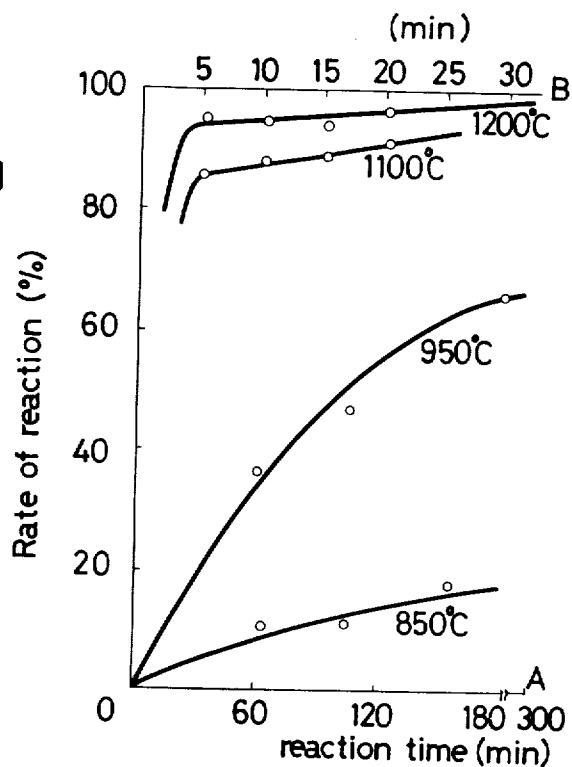


Fig. 2

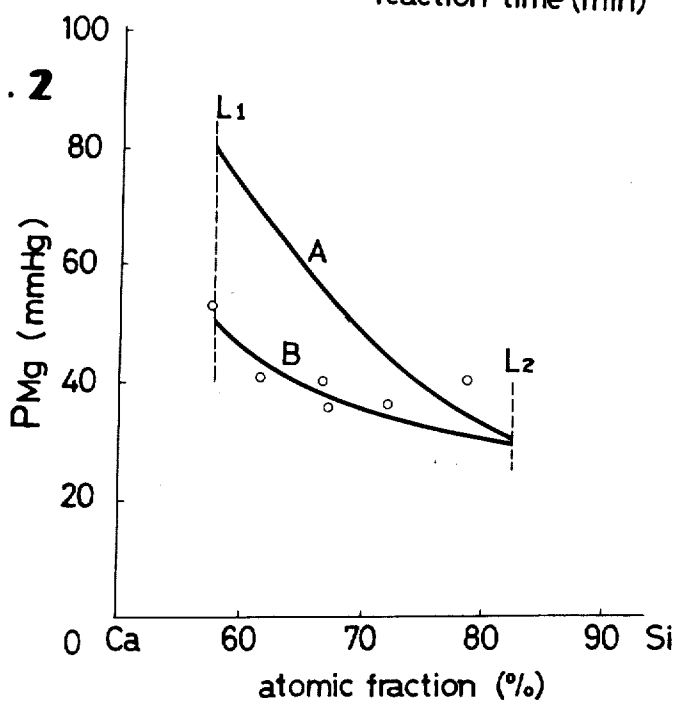


Fig. 3

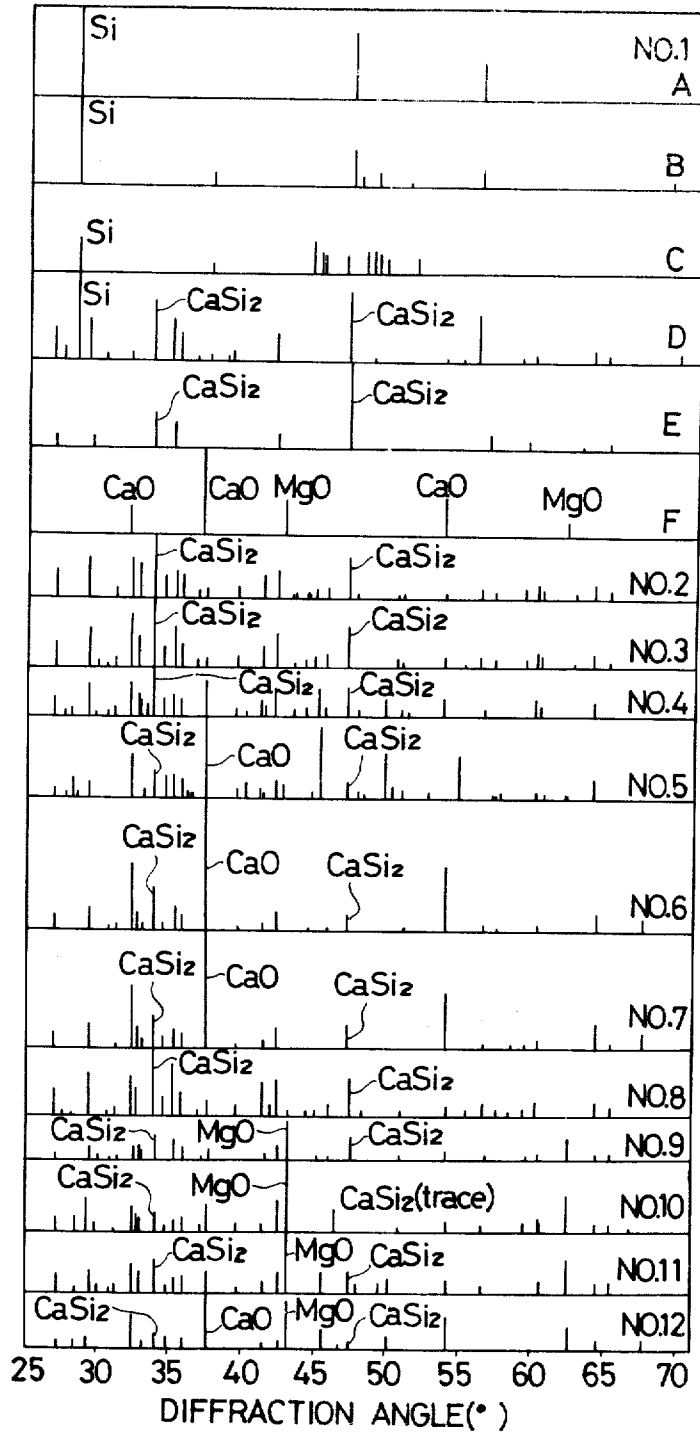


Fig. 4

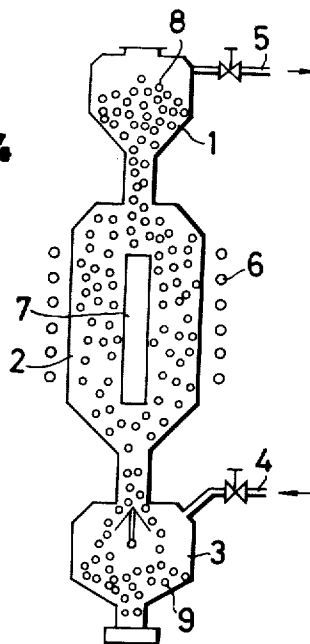


Fig. 5

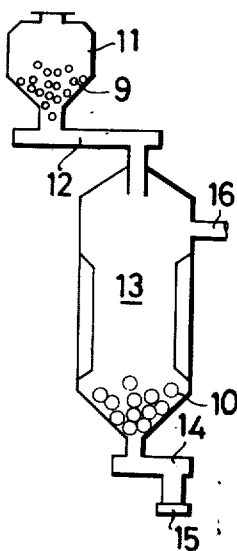


Fig. 6

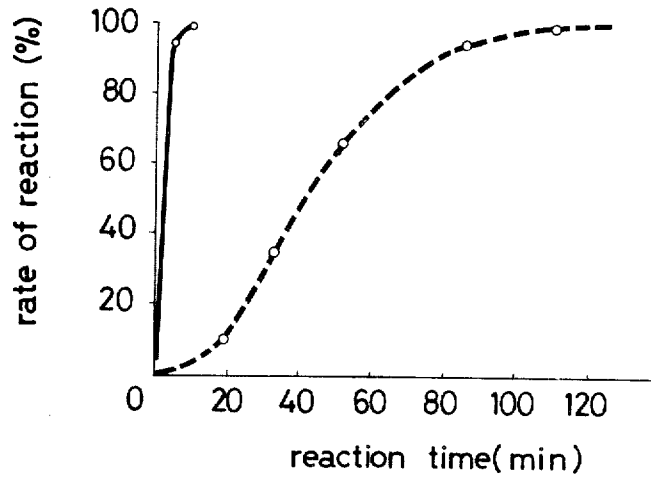
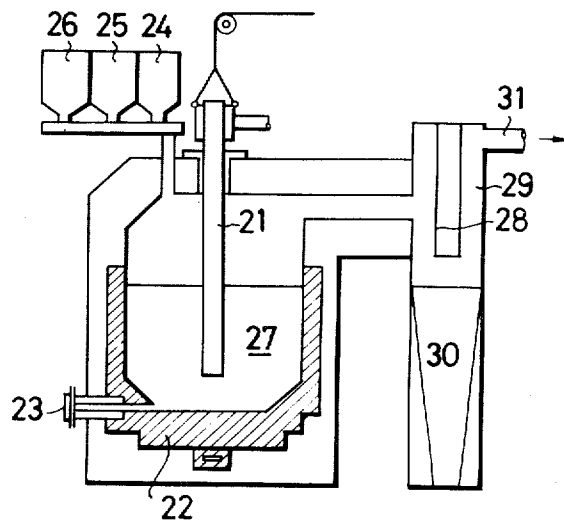


Fig. 7



PROCESS FOR PRODUCTION OF MAGNESIUM

BACKGROUND OF THE INVENTION

This invention relates to an improved process for the production of metallic magnesium by the thermic reduction of magnesium oxide at an elevated temperature.

Commercial methods employed for the manufacture of metallic magnesium are divided under two classes, i.e., electrolytic methods which obtain magnesium by the electrolysis of magnesium chloride ($MgCl_2$) and thermic reduction methods, which produce magnesium vapor by thermally reducing magnesium oxide in a vacuum.

The present invention relates to a vacuum reduction method and, more particularly, to the silicothermic reduction method.

These methods reduce calcined natural dolomite or calcined artificial dolomite (mixture of magnesium oxide and calcium oxide) at an elevated temperature under a high degree of vacuum by using chiefly silicon or silicon-iron alloy as the reducing agent and condense the resultant vaporized magnesium to obtain metallic magnesium in a solid or liquid form. These operations are batchwise. The reaction of reduction is effected by the Pidgeon Process in an externally heated steel-made retort under conditions of about $1200^{\circ}C$ and 10^{-2} mmHg and by the Magnetherm Process in an internally heated vacuum electric furnace under conditions of above $1500^{\circ}C$ and 20 mmHg, for example. The reduction reaction gives birth to a reaction residue, which is discharged in the form of a high-temperature solid in the case of the Pidgeon Process and in the form of a high-temperature molten slag in the case of the Magnetherm Process. The capacity for magnesium production per unit reactor, namely one retort in the Pidgeon Process or one electric furnace in the Magnetherm Process, is 50 to 90 kg/day or 2.5 to 7.5 tons/day. Thus, the unit capacity is much greater by the Magnetherm Process. According to the Magnetherm Process, the reaction residue is discharged in the form of a high-temperature molten slag and, owing to addition of alumina to the raw materials, the melting point of the reaction residue is lowered so that at the working temperature of the electric furnace, the reaction residue retains a molten state possessed of suitable electric conductivity. Said reaction residue, therefore, constitutes itself an electric resistor and, because of the Joule effect, functions as an internal heat source of the electric furnace. Further, the molten slag can easily be discharged by means of tapping procedure. Because of these advantages, this process permits use of a large capacity electric furnace.

Even with the Magnetherm Process, however, it is difficult to achieve improved efficiency over the existing level for the reasons to be given herein below. In the Magnetherm Process, a granular magnesia-containing substance and a granular reducing agent are added intermittently to the molten slag and dissolve therein to cause a reaction of reduction in the molten slag. It is clear from physical chemical theory regarding molten substances that the rate of the reaction depends on the activity of MgO in the molten slag. As the reaction proceeds, the reaction velocity declines and the yield of magnesium decreases.

An object of this invention is to provide an improved process of notably high yield for the manufacture of

magnesium by the dry thermic reduction of magnesium oxide.

SUMMARY OF THE INVENTION

To accomplish the object described above according to the present invention, there is provided a process which comprises, as a first stage, blending a substance composed of magnesium oxide and calcium oxide, generally known as dolomite, with silicon or ferrosilicon or a mixture thereof, shaping the blend in the form of briquets, subsequently heating the briquets in an inert atmosphere under temperature and pressure conditions capable of substantially inhibiting formation of magnesium vapor, said temperature being not lower than the melting temperature of calcium-silicon alloy, and thereby forming calcium-silicon alloy within said briquets, and, as a second stage, placing the briquets containing the calcium-silicon alloy in a steel retort or tightly closed electric furnace and heating the briquets therein to produce magnesium vapor. The magnesium vapor is solidified at a cooled section of the steel retort or it is introduced into a separate condenser to be liquefied. The briquets having calcium-silicon alloy formed therein are hard enough to resist disintegration and show high thermal conductivity. Particularly the fact that magnesium oxide and the calcium-silicon alloy are held in a state of intimate contact within the briquets brings about highly advantageous conditions for the reduction reaction. Since the reaction velocity is notably high, the rate of reaction achieved is high and the vapor pressure of magnesium is also high as compared with those obtained by known methods, there is enjoyed an advantage that the operation can be performed not only under a pressure above normal pressure but even under a pressure even below normal pressure, the production rate or yield of magnesium is higher than that of known methods and production can be made more economical.

The other characteristics and advantages of the present invention achieved to success from the detailed description to be given herein below with reference to the attached drawings.

BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a graph showing the results of a test conducted on the rate of reaction in the formation of calcium-silicon alloy by the reaction between calcium oxide from calcined dolomite and silicon.

FIG. 2 is a graph showing the relation between the atomic fraction of Ca and Si and the vapor pressure of magnesium observed in the reduction of magnesium oxide with calcium-silicon alloy.

FIG. 3 represents X-ray diffraction patterns substantiating presence of reactants and products described in the specification of this invention.

FIG. 4 is a reaction apparatus used in Example 1 for calcining crude briquets.

FIG. 5 is a reducing apparatus used in Example 1 and Comparative Example 1.

FIG. 6 is a graph showing the relation between the reaction time and the rate of reaction determined in Example 1 and Comparative Example 1.

FIG. 7 is a reducing apparatus used in Example 2 and Comparative Example 2.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to improvements pertaining to and in the method for the manufacture of magnesium

3

by the silicothermic reduction of calcined dolomite.

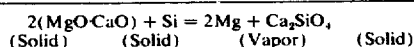
This invention originates in the mechanism of reaction newly brought to light by the inventors and is concerned with a process for the production of magnesium by the thermic reduction of calcined magnesium oxide with silicon accomplished at an efficiency higher than is obtained by known methods.

Now, the present invention will be described in detail.

The term "calcined dolomite" used herein below in the description shall be interpreted as either calcined natural or artificial dolomite containing magnesium oxide and calcium oxide substantially equimolarly and products obtained by calcining mixture of magnesium oxide with calcium oxide and mixtures thereof with carbonates or hydroxides. The term "inert gas" shall refer to gases which refrain from reacting with other coexisting substances in the course of a reaction. Specifically for the purpose of the present invention, argon, neon, helium and hydrogen are used either singly or in the form of a mixture as the inert gas.

First, the mechanism of reaction brought to light and forming the foundation of the present invention will be described with reference to the results obtained in test.

1. It has heretofore been held that the solid-phase reduction of calcined dolomite by silicon proceeds because the calcined dolomite and silicon react directly with each other to produce dicalcium silicate, as expressed by the following reaction formula, and consequently increase the absolute value of the free energy of reaction which is required for the reduction of magnesium oxide.



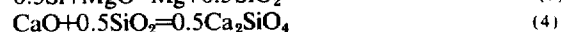
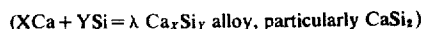
The inventors have demonstrated, however, that in the reaction of calcined dolomite with silicon, magnesium oxide from the calcined dolomite is not reduced directly by silicon but calcium-silicon alloy is formed first by the reaction of calcium oxide with silicon and the reduction reaction between magnesium oxide and this alloy proceeds subsequently.

The test results covering the reaction velocity in the formation of the calcium-silicon alloy by the reaction between the calcium oxide from the calcined dolomite and silicon are shown in FIG. 1. Powdered calcium oxide and silicon were intimately blended in amounts to give a ratio of 4 mol of CaO to 5 mol of Si sufficient for producing calcium silicon alloy particularly calcium disilicide (CaSi₂) by reducing calcium oxide from the calcined dolomite without excess or deficiency and the resultant blend was shaped in the form of briquets having an apparent density of about 1.4 to 2.2. The sample briquets were heated in an inert atmosphere of argon at varying temperatures of 850°, 950°, 1100° and 1200°C for a prescribed time. The heating was carried out in a high-frequency furnace for the temperature of briquets to be elevated quickly to the indicated levels, so that the initial conditions of reaction and their possible effects were negligible. Yields of CaSi₂ were determined by X-ray diffraction analysis and differential thermal analysis. In the graph of FIG. 1, the rate of reaction in the formation of CaSi₂ is indicated by the ordinate and the reaction time (in minutes) by the abscissa. The coordinates for the temperatures of 1100° and 1200°C

4

correspond to the upper abscissa graduation and those for the temperatures of 950° and 850°C to the lower abscissa graduation respectively. It is seen from the graph that the reactions at 1100° and 1200°C proceed very quickly so that within only 5 minutes of reaction, the ratio of formation of CaSi₂ exceeds 85% at 1100°C and 95% at 1200°C respectively. In contrast, the reactions at 850° and 950°C proceed very slowly. A possible reason for the significant difference in the rate of reaction between the temperature levels of 950° and 1100°C may be that at temperatures over about 1050°C, the formed alloy is in a molten state and the reaction taking place in a solid-liquid phase proceeds at a notably high reaction velocity, whereas at temperatures under 950°C, the alloy is in a solid form and does not contribute to acceleration of the reaction at all.

The present invention resides in applying what the inventors have thus brought to light to the process for magnesium production. The reaction of the calcium-silicon alloy with the calcined dolomite proceeds in the paths expressed by the following elementary reaction formulas (1) through (4).



$$P_{Mg} = (P_{Mg}^{Ca-Si})^{\frac{2m}{2m+n}} (P_{Mg}^{Ca})^{\frac{n}{2m+n}} \quad \text{(present formula)}$$

In these reactions, it does not matter whether the substances involved, except the magnesium vapor produced, are in a molten state or in a solid state. The results brought to light by the inventors can be explained by the associated reaction formula.

Thus, the vapor pressure of magnesium is represented in accordance with reaction (2) through (4). P_{Mg} denotes the vapor pressure of magnesium, a_{Si} the activity of silicon and a_{Ca} the activity of calcium respectively.

By using a preparation having magnesium oxide and calcium oxide mixed at a desired ratio, namely a preparation in which the variables m and n in the aforementioned formulas are selected as desired, as well as by using dolomite, it is made possible to form a calcium-silicon alloy of the desired composition and then to accomplish the reduction of magnesium, with the vapor pressure of magnesium controlled as desired.

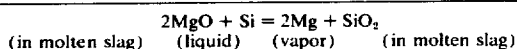
The variables n and m are reaction fractions of the formulae (2) and (3) respectively. Accordingly, m/n equals the ratio of the corresponding elementary reactions.

2. The conclusion indicated by the present formula has been confirmed through tests conducted with a view to formulating a specific process capable of materializing what the inventors have brought to light. FIG. 2 shows the results. Sample briquets having an apparent density of about 1.8 were prepared by mixing magnesium oxide, calcium oxide and calcium-silicon alloy having a different Si/Ca atomic ratio, and shaping the blends. For the purpose of comparison with the Pid-

geon Process in which activities of the oxides are in unity, the reaction temperature was fixed at 1200°C and the heating was given in a stream of argon to measure the equilibrium pressure of magnesium vapor. In the graph of FIG. 2, the ordinate indicates the vapor pressure of magnesium in mmHg (P_{Mg}) and the abscissa indicates the atomic fraction of Ca and Si. In the graph, A represents thermodynamically calculated values and B experimentally found values. L_1 is liquidus point of the alloy in which the primary precipitation of Ca—Si occurs, L_2 is liquidus point of the alloy in which the primary precipitation of Si occurs. The deviation of B from A results from the fact that thermodynamic data under consideration are presumably not settled. In the curve of B, the observed value of vapor pressure at the atomic fraction of 0.667Si and of 0.333Ca is found to be approximately equal to the condition expressed by the reaction formula of the Pidgeon Process and this vapor pressure is in agreement with the value observed by investigators. Both the experimentally and thermodynamically determined curves show that the vapor pressure versus composition depends upon the content of calcium.

3. Then, a study was made of the relation between the reaction temperature and the vapor pressure of magnesium. Calcined natural dolomite (containing 31.8% by weight of MgO) and metallic silicon were pulverized to a particle size of finer than 80 mesh, blended in amounts to give a molar ratio MgO/Si=2/1 and shaped in the form of briquets having an apparent density of about 2.0 g/cm³. The sample briquets were preliminarily heated in the atmosphere of argon under normal pressure at 1200°C for five minutes to cause formation of calcium-silicon alloy within the briquets. Then the heated briquets were cooled and crushed into grains 3 to 5mm in diameter. By the same method as described above, the sample grains thus obtained were tested for equilibrium pressure of magnesium vapor. Consequently, there were obtained notably high vapor pressures such as, for example, 70 mmHg at 1250°C, 180 mmHg at 1350°C, 400 mmHg at 1450°C and 1330 mmHg at 1600°C, clearly indicating a relation of $\log P = A/T + B$ between the logarithmic vapor pressure and the reciprocal of absolute temperature, the parameters being $A = -10,454$ and $B = 8.706$. According to this formula, the reaction temperature required for the vapor pressure of magnesium to reach 760 mmHg in this reaction system is calculated to be about 1520°C.

In contrast, the principle of the reaction involved in the operation of the Magnetherm Process is expressed by the following formula (5), indicating that the reduction of MgO depends on the activity of Si contained in the silicon-iron alloy used as the reducing agent and on the activity of MgO present in the multicomponent molten slag.



$$\log P_{Mg} = \log P_{Mg}^{\circ} a_{Si}^{1/2} \cdot a_{MgO} \cdot a_{SiO}^{-1/2}$$

wherein, P_{Mg} denotes the vapor pressure of magnesium, P_{Mg}° denotes the vapor pressure of magnesium of standard state thermodynamically, and a_{Si} , a_{MgO} , a_{SiO} denote the activities of Si, MgO and SiO respectively.

From the standpoint of the melting point of molten slag, however, it is difficult to maintain reasonably high activity of MgO to improve the vapor pressure of magnesium under consideration. In the neighborhood of 1600°C, the vapor pressure of magnesium is at most several tens of mmHg when the slag composition is that of normal operation according to the formula (5). According to the present invention the process can be operated at a notably high vapor pressure of magnesium which is established by the reaction under consideration. This advantage brings about an effect of inhibiting subsidiary reaction products such as CO and SiO which pose a serious problem to the Magnetherm Process.

4. Further, the production of calcium-silicon alloy can be obtained by using ferrosilicon instead of silicon. It has been demonstrated by X-ray diffraction analysis that in the substitute use, silicon corresponding to the amount of silicon resulting from the deduction of the compound equivalent to FeSi₂ in the case of 75% ferrosilicon and that from the deduction of the compound equivalent to FeSi in the case of 50% ferrosilicon respectively take part in the reaction preferentially.

FIG. 3 represents X-ray diffraction patterns obtained by reactants and products in the various tests mentioned above. Specifically, the diagrams No. 1 A through F are standard diffraction lines used to detect reactants and products. The diagram A represents use of pure silicon and the diagram B use of 75% ferrosilicon; in the range of the used composition, FeSi₂ is also detected. The diagram C represents use of 50% ferrosilicon, although presence of FeSi is detected besides the compound mentioned above. The diagram D represents a calcium-silicon alloy having a composition of 62.9% of Si, 30.1% of Ca and the remainder of Fe. The diagram E represents use of calcium disilicide prepared stoichiometrically. The diagram F represents use of calcined dolomite as the raw material. The diagrams No. 2 through No. 5 relate to briquets which were stoichiometrically prepared, with the aim of producing CaSi₂, to include calcium oxide and pure silicon or 90%, 75% or 50% ferrosilicon at a molar ratio of said CaO to free silicon of 4 to 5 and which were thereafter subjected to heat treatment in the first stage to produce CaSi and accompanying Ca₂SiO₄ so that unreacted Si is recognizable. The diagrams No. 6 and No. 7 represent the preparations having calcium oxide and silicon blended in amounts to give a molar ratio CaO/Si=4/3 and 4/2 respectively, each having silicon content of less than is stoichiometrically required. Substantially the whole of the silicon is seen to have taken part in the reaction, with diffraction lines of CaSi₂ and excess CaO appearing conspicuously. Similar results have been confirmed to issue from the reaction between calcined dolomite and silicon. The diagrams No. 9 through No. 12 represent the briquets having a molar ratio of CaO/Si=4/5, with pure Si, 90% ferrosilicon, 75% ferrosilicon and 50% ferrosilicon respectively used as the reducing agent. The diagrams furnish a clear proof that silicon does not react with magnesium oxide directly but reacts preferentially with calcium oxide to produce CaSi₂.

The present invention has been accomplished on the basis of the results brought about from the various tests described above. To be more specific, this invention relates to a process which comprises, as a first stage, adding silicon or ferrosilicon to calcined dolomite or a magnesium-containing raw material having magnesium

de mixed with calcium oxide, homogeneously blended and shaping the mixture in the form of briquets, heating the briquets in an inert atmosphere under the temperature and pressure conditions capable of substantially inhibiting the formation of magnesium vapor thereby giving rise to calcium-silicon alloy within the briquets and, as a second stage, heating the briquets containing the calcium-silicon alloy to effect the reduced reduction. In this case, the briquets are generally prepared by pulverizing natural or artificial dolomite and silicon or ferrosilicon to a particle size finer than 80 mesh and blending the resultant powders. For practical purpose, the raw materials are desired to be mixed at a stoichiometric ratio or roughly at a molar ratio $MgO/CaO/Si=1/1/0.5$. In this case, the equimolar ratio $MgO/CaO=1/1$ is practically satisfied in natural dolomite. Where ferrosilicon is used as the silicon source, it is adequate to determine the amount of ferrosilicon so as to meet the aforementioned molar ratio in terms of free silicon equivalent. The briquets thus prepared are then heated. As regards the temperature for heating, since the ratio of reaction is extremely low, temperatures under $950^{\circ}C$ as indicated in FIG. 1, the lower limit of reaction temperature is fixed at $50^{\circ}C$. The upper limit of temperature for this heating must satisfy the conditions capable of substantially inhibiting the formation of magnesium vapor during the heating. Said conditions are selected from the formula expressing the relation between the temperature and the vapor pressure of magnesium touched upon in (3) of the results of test described above. Let T_1 stand for the absolute temperature required for heating the briquets under normal pressure, and the pressure (in mmHg) is required to exceed the value of P_1 which is calculated from the following equation.

$$\log P_1 = \frac{-10.454}{T_1} + 8.706$$

For example, the heating is given advantageously at a temperature of about $1500^{\circ}C$ under normal pressure and of about $1200^{\circ}C$ under a reduced pressure of about 25 mmHg. If the briquets are heated at the temperature satisfying the conditions just described, then the reaction leading to the formation of calcium-silicon alloy is accelerated, the formed calcium-silicon alloy is obtained in a molten state, the briquets consequently acquire hardness enough to withstand disintegration, the thermal conductivity is enriched, the magnesium oxide and the reducing agent in the briquets are brought into a state of intimate contact and conditions highly advantageous for the reducing reaction in the subsequent step are brought about. The briquets are subsequently subjected to solid-phase reduction in the following step. If, in this case, they are exposed to a temperature exceeding the melting point of the calcium-silicon alloy retained therein, or even after they have thoroughly released magnesium vapor, the briquets themselves are melted fast by the magnesium oxide or the high melt-dicalcium silicate resulting from the reduction and, therefore, are kept from being disintegrated.

Now a description will be given of the reduction to which the briquets containing the calcium-silicon alloy are subjected. The reaction conditions (temperature and pressure) for this reduction can be selected in accordance with the vapor pressure of magnesium and the reaction velocity. Specifically, the heating is re-

quired to be given under a pressure lower than the pressure which is calculated from the formula of the relation between the pressure P (mmHg) and the absolute temperature T touched upon in (3) of the test results described above. Let T_2 stand for the absolute temperature of heating, and the pressure will have to be lower than the pressure P_2 (in mmHg) to be calculated from the following equation.

$$\log P_2 = \frac{-10.454}{T_2} + 8.706$$

In the operation of the Pidgeon Process or the Magnetherm Process, the equilibrium pressure of magnesium vapor at the operation temperature is of the order of several tens of mmHg at most. The countertype of the present invention plainly exceeds this level. The lower limit of the temperatures at which the present invention can manifest its characteristic features should, therefore, be fixed at $1200^{\circ}C$ (the temperature at which the equilibrated pressure of magnesium vapor exceeds 40 mmHg). As is evident from (3) of the test results introduced above, the equilibrium pressure of magnesium vapor notably increases as the temperature raises from the limit $1200^{\circ}C$ and the degree to which the operating pressure within the reaction system is decreased can be mitigated in proportion as the temperature increases over this level. If the reduced pressure is maintained, then the reduction is accelerated and the productivity is improved accordingly. In practical operation, therefore, it is desirable to use as low a pressure as permissible insofar as the pressure is not below the equilibrated pressure of CO gas. Normally, the reaction can be carried out under a pressure above 25 mmHg. Conditions desirable for obtaining high productivity are 5 to 10 mmHg at $1200^{\circ}C$ and 50 to 100 mmHg at $1500^{\circ}C$, for example. As concerns the upper limit of temperature for the reduction reaction, no restrictive factor arises from the reaction itself. It is determined by such factors as the durability of the reaction system to heat and the thermal stability of the molten slag. With a view to permitting the mineral slag to be discharged in a molten stage, therefore, the upper limit of temperature determinable from the data on phase diagram of mineral slag is $1700^{\circ}C$.

When the briquets having the calcium-silicon alloy formed therein are placed within the heating furnace kept at $1200^{\circ}C$ to $1700^{\circ}C$, the reduction of magnesium oxide by the calcium-silicon alloy is carried out very rapidly and a major amount of magnesium vapor is evolved. Then the magnesium vapor is introduced to the condenser and collected in the liquid state. If an internally heated furnace is employed as the heating furnace, the molten slag is retained continuously within the furnace throughout the continuous operation thereof. Depending on the nature of the briquets and on the nature of the molten slag, the briquets having the calcium-silicon alloy formed therein at times float on the surface of the molten slag or may be partially or totally submerged in the molten slag, and complete the magnesium production with notably high vapor pressure of magnesium.

This concludes the description of the present invention. It is further pointed out that since the process of this invention can be exercised at a degree of vacuum milder than that involved in the operation of the known methods such as, for example, the Pidgeon Process and

the Magnetherm Process, it enjoys the following advantages.

The fact that the process of this invention can be carried out at a mild degree of vacuum while the other methods require operations to be performed at such a greatly reduced pressure as 10^{-2} mmHg brings about an effect of inhibiting the formation of CO gas or SiO gas in the furnace interior and of eliminating the degradation of magnesium yield of the accelerated wear of electrodes due to reoxidation of formed magnesium vapor. With reference to the reaction between molten slag and the electrode or lining carbon as experienced by the Magnetherm Process, since the equilibrium pressure of CO at 1500° to 1600°C is more than about 17 mmHg, the surface of the carbon electrode or carbon lining within the furnace is covered with a film of CO gas under such degree of vacuum as saved 10 or 20 mmHg applied in the case of the Magnetherm Process which results in the loss of energy, increased electrode load and attendant obstacles and reoxidation of magnesium. The process of this invention does not require the furnace interior to be maintained under a high degree of vacuum and, therefore, does not entail the various obstacles just mentioned.

As is demonstrated by the preferred embodiments of this invention, the process of this invention, when carried out by using such furnace as is employed in practicing the Magnetherm Process, Pidgeon Process or some other similar known process, brings about a notable improvement in the productivity and yield of magnesium permits continuous feeding of raw materials provides effective inhibition of harmful secondary reactions, and so on.

The heat treatment in the first stage and all the treatments in the second stage according to the method of the present invention can be carried out in one furnace by using an internally heated furnace containing therein a molten slag and having such a construction that the crude briquet to be cast into the furnace forms therein a calcium-silicon alloy before it reaches the molten slag, and the resultant briquet reaches the molten slag.

Now the present invention will be described more specifically herein below by reference to preferred embodiments. It should be noted, however, that the present invention is not limited to these examples.

EXAMPLE 1

Calcined natural dolomite (containing 31.8% by weight of MgO) pulverized to a particle size finer than 80 mesh and 75% ferrosilicon (containing 49.5% of free silicon) pulverized to a particle size finer than 80 mesh were mixed in amounts to give a molar ratio $\text{MgO/Si}=2/1$ to $2/1.1$ and the blend was shaped in the form of crude briquets having an apparent specific gravity of about 2.0 g/cm^3 and a maximum diameter range of $\pm\text{mm}$ to 40mm .

Then, the crude briquets were placed in a reaction apparatus like the one shown in FIG. 4 and heated therein.

In the drawing, 1 denotes an upper hopper, 2 a reaction zone, 3 a briquet receptacle, 4 and 5 a gas inlet and outlet, 6 an external auxiliary heater, (with a metal or carbon serving as a heating element; a proper external gas flame heater or electric resistance generator may be used as occasion demands) 7 a high-frequency generator, 8 crude briquets and 9 briquets having calcium-silicon alloy formed therein. In the present example,

argon was introduced as the inert gas through the inlet 4 and discharged through the outlet 5 to effect displacement of the air in the reactor interior. The heating of the briquets for the formation of said calcium-silicon alloy was carried out under a minute pressure (several mm of water column) of this inert gas. To be specific, when the crude briquets 8 were fed to the upper hopper 1, they were caused to descend down the reaction zone 2 (kept at 1050° to 1200°C), during which descent they were heated by the high-frequency wave generator 7 and consequently caused to produce calcium-silicon alloy therein. The fired briquets 9 containing the calcium-silicon alloy were then moved into the briquet receptacle 3. As is apparent from the diagram, the heating or the formation of calcium-silicon alloy in the briquets could be carried out continuously by having crude briquets fed continuously into the upper hopper 1.

When the retention time of the briquets within the reaction zone was fixed at about 20 minutes, the conversion to calcium-silicon alloy exceeded 95%.

Subsequently the fired briquets having the calcium-silicon alloy already formed therein were subjected to reduction reaction in a reduction apparatus like the one shown in FIG. 5. In the drawing, 9 denotes the fired briquets, 10 the slag, 11 a raw material bin, 12 a screen feeder, 13 an internally heating reaction furnace, 14 a screw, 15 a slag discharge outlet and 16 a magnesium vapor outlet.

The fired briquets 9 stored in the raw material bin 11 were conveyed by the screw feeder 12, thrown into the internally heated reaction furnace 13 and retained for a fixed length of time in the furnace interior. The solid slag formed was discharged by the screw 14 through the outlet 15. Inside this furnace, the fired briquets were heated and MgO in the briquets was reduced to give rise to magnesium vapor. The furnace interior was maintained under conditions of 10^{-2} to 10^{-3} mmHg of pressure and 1300°C of temperature.

Of the results obtained in this example, the relation between the reaction time and the rate of reaction (calculated on the basis of MgO remaining in the solid slag) was as shown in FIG. 6. In the graph, the ordinate represents the rate of reaction (%) and the abscissa the reaction time (minutes). The continuous line represents the results obtained in this example. The graph indicates that the rate of reaction over 95% was reached very rapidly, namely in a matter of 5 to 10 minutes.

COMPARATIVE EXAMPLE 1

Crude briquets prepared by faithfully following the procedure of Example 1 were at once placed in the reducing apparatus of FIG. 5 as used in Example 1 and subjected to reducing reaction. The results are shown by the dotted line in the graph of FIG. 6.

As the graph clearly indicates, a reaction time of more than 90 minutes was required for the rate of reaction to exceed 95%. The briquets involved in the present comparative example exhibited a behavior entirely the same as that observed in the operation of the Pidgeon Process. Comparison clearly shows that the process of the present invention is effective in notably improving the productivity and yield of magnesium as evidenced by the results of Example 1.

EXAMPLE 2

The procedure of Example 1 was followed by using entirely the same raw materials to produce briquets

having calcium-silicon alloy formed therein. The fired briquets were then subjected to reduction reaction by using an apparatus like the one shown in FIG. 7 under the various conditions described hereinbelow.

In the drawing, 21 denotes a vertically movable electrode, 22 a carbonaceous furnace base, 23 a tap for the molten mineral slag, 24, 25 and 26 each a briquet bin, 27 the molten mineral slag composed preponderantly of $\text{Ca}_2\text{SiO}_4\text{--Al}_2\text{O}_3$ system, 28 a magnesium vapor pump, 29 a magnesium vapor condenser, 30 a magnesium receptacle and 31 an air discharge outlet. The apparatus shown in FIG. 7 is an improved vacuum-tight, single-electrode furnace whose electrode is rendered vertically movable under reduced pressure.

In the present example, the reaction ratio was studied under various conditions by changing the feed rate of raw materials, with the furnace interior maintained under 50 mmHg of pressure and 1400° or 1500°C of temperature. The results of the test are shown in the accompanying table under the columns, B-1 through B-5. In the test, the actual power load was 48 to 55 KW/kg.Mg/hr. The reaction ratio was calculated on the basis of the yield of magnesium.

COMPARATIVE EXAMPLE 2

An apparatus like the one shown in FIG. 7 and described in Example 2 was used, calcined natural dolomite (containing 37.4% by weight of MgO and 59.7% by weight of CaO) coarsely crushed into grains 5 to 14mm in diameter was thrown into the bin 24, 80% ferrosilicon coarsely crushed into grains 5 to 14mm in diameter was fed into the bin 25 and powdered alumina prepared by the Bayer Process for use in electrolysis of aluminum was introduced into the bin 26. They were blended to a regulated composition and treated in accordance with the Magnetherm Process. To be specific, the calcined natural dolomite, ferrosilicon and alumina were blended in amounts to give a weight ratio of 77/14/9 and fed into a molten slag (consisting of 54.8% of CaO, 28.5% of SiO_2 , 15% of Al_2O_3 , and 1.5-2% of

curring a phenomenon of shelving around the upper electrode. No increase of actual power load resulted in operational improvement.

The results of Example 2 and those of Comparative Example 2 are compared in the table. This table furnishes a clear proof that the effects of the present invention are conspicuous. The data of B series are seen to be superior to those of A clearly in terms of consumption of raw materials, feed rate of raw materials, yield of magnesium (kg/hr.) and reaction ratio of magnesium.

EXAMPLE 3

Briquets having calcium-silicon alloy formed therein were prepared by faithfully following the procedure of Example 1. These briquets were subjected to operations performed under varying magnitudes of pressure not lower than normal pressure. According to (3) of the results of test described in the detailed description, the temperature at which the equilibrium pressure of magnesium vapor issuing from the briquets of this invention reaches 760 mmHg is calculated to be about 1520°C. Actually in the present example, however, the reaction temperature was fixed at 1600°C. At this reaction temperature, the vapor pressure of magnesium reached 1330 mmHg, a value amply sufficient for smooth progress of the reaction.

In this example, the vacuum system was so controlled that the inner pressure of the reaction apparatus reached 760 mmHg and 1100 mmHg during the operation. The results of the operation were as shown in the table under the column, B-6 and B-7. The actual electric power against the reaction was invariably about 5.5 KW/kg.Mg/hr. As the results indicate, the operation of the present invention could be carried out when the apparatus interior pressure is higher than normal pressure. In this case, both productivity and reaction ratio were decidedly higher than could be obtained by the conventional process (data under the column A, in the same table).

Table

	A	B-1	B-2	B-3	B-4	B-5	B-6	B-7
Reaction temperature (°C)	1500	1400	1500	1500	1500	1500	1600	1600
Pressure (mmHg)	10	50	50	50	50	50	760	1100
Feed rate of raw materials (kg/hr)	625	640	726	869	1169	1895	1780	1125
Feed rate of raw Mg (kg.Mg/hr)	107	108	123	147	198	321	302	191
*Ratio of feed rate of raw material	1.0	1.02	1.16	1.39	1.87	3.03	2.78	1.80
Yield of Mg (kg.Mg/hr)	92.0	94.2	114.6	142.0	189.5	294.0	302.0	182.0
Reaction ratio of Mg (%)	86.0	87.2	93.2	96.6	95.7	91.6	96.5	95.3

*The values for the B series are those proportionate to the value (625 kg/hour) for A.

MgO) in the furnace interior at the rate of 625 kg/hour (introduced batchwise at intervals of 12 minutes) and allowed to react under conditions of 1500°C of temperature and 10 mmHg of pressure. The results were as shown in the table under the column A. In this case, the magnesium reaction ratio determined by the same method as in Example 1 was 86% and the actual electric power against the reaction was 6.5-7.8 KW/kg.Mg/hr. In this case, when the feed rate of raw materials was increased, the reaction became remarkably unstable and, owing to consequent solidification of slag and segregation of raw materials and slag, there oc-

What is claimed is:

1. In a process for obtaining metallic magnesium from a mixture of magnesium oxide with calcium oxide as the raw material by reducing said mixture at an elevated temperature to give rise to magnesium vapor and cooling said magnesium vapor, the improvement which comprises two stages, the first stage of adding at least one member selected from the group consisting of silicon and ferrosilicon to said mixture consisting of magnesium oxide and calcium oxide, blending and shaping the resultant mixture in the form of briquets, and heating said briquets in an inert atmosphere under tempera-

13

ture and pressure conditions capable of substantially inhibiting the formation of magnesium vapor, said temperature being not lower than the melting point of calcium-silicon alloy and thereby giving rise to calcium-silicon alloy within said briquets and the second stage of heating, in a heating furnace, the briquets having calcium-silicon alloy formed therein for thereby reducing the magnesium oxide present in said briquets into metallic magnesium.

2. The process of claim 1, wherein said heating furnace is an internally heated furnace containing therein a molten slag and having such a construction that the crude briquets to be cast into the furnace are heated to each form therein a calcium-silicon alloy before they reach the molten slag, and the resultant briquets reach the molten slag so as to allow the reduction of magnesium oxide, in which the heat treatment in the first stage and all the treatments in the second stage are carried out.

3. The process of claim 1, wherein the heating in the first stage is given at a temperature in the range of from 1050° to 1500°C under a pressure exceeding the pressure calculated from the formula:

$$\log P_1 = \frac{-10,454}{T_1} + 8.706$$

(wherein, P₁ denotes the pressure expressed in mmHg and T₁ is said heating temperature) in an inert atmosphere.

14

4. The process of claim 3, wherein the heating in the first stage is carried out in an atmosphere of argon at a temperature in the range of from 1050° to 1200°C for a period between 5 and 20 minutes.

5. The process of claim 1, wherein the briquets having calcium-silicon alloy formed therein are heated at a temperature in the range of from 1200° to 1700°C under a pressure not higher than the pressure calculated from the formula:

$$\log P_2 = \frac{-10,454}{T_2} + 8.706$$

(wherein, P₂ its the pressure expressed in mmHg and T₂ is said heating temperature) in a gaseous atmosphere wherein at least one member selected from the group consisting of an inert gas and magnesium gas.

6. The process of claim 5, wherein the heating furnace is an internally heated furnace containing a molten slag, the pressure of the inert atmosphere is at least 25 mmHg, and the briquets having calcium-silicon alloy formed therein are heated in a state such that the briquets float on said molten slag.

7. The process of claim 5, wherein the heating furnace is an internally heated furnace containing a molten slag, the pressure of the inert atmosphere is at least 25 mmHg, and the briquets having calcium-silicon alloy formed therein are heated in a state such that the briquets are wholly or partially submerged in said molten slag.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,918,959 Dated November 11, 1975

Inventor(s) Tomoo Matsushima et al. Page 1 of 4

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

Column 7, should appear as shown on the attached sheets.

Signed and Sealed this
twenty-seventh Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

oxide mixed with calcium oxide, homogeneously blending and shaping the mixture in the form of briquets, heating the briquets in an inert atmosphere under the temperature and pressure conditions capable of substantially inhibiting the formation of magnesium vapor and thereby giving rise to calcium-silicon alloy within the briquets and, as a second stage, heating the briquets containing the calcium-silicon alloy to effect the required reduction. In this case, the briquets are generally prepared by pulverizing natural or artificial dolomite and silicon or ferrosilicon to a particle size finer than 80 mesh and blending the resultant powders. For practical purpose, the raw materials are desired to be mixed at a stoichiometric ratio or roughly at a molar ratio $MgO/CaO/Si = 1/1/0.5$. In this case, the equimolar ratio $MgO/CaO = 1/1$ is practically satisfied in natural dolomite. Where ferrosilicon is used as the silicon source, it is adequate to determine the amount of ferrosilicon so as to meet the aforementioned molar ratio in terms of free silicon equivalent. The briquets thus prepared are then heated. As regards the temperature for this heating, since the ratio of reaction is extremely low at temperatures under $950^{\circ}C$ as indicated in Fig. 1, the lower limit of reaction temperature is fixed at $1050^{\circ}C$. The upper limit of temperature for this heating must satisfy the conditions capable of substantially inhibiting the formation of magnesium

vapor during the heating. Said conditions are selected from the formula expressing the relation between the temperature and the vapor pressure of magnesium touched upon in (3) of the results of test described above. Let T_1 stand for the absolute temperature required for heating the briquets under normal pressure, and the pressure (in mmHg) is required to exceed the value of P_1 which is calculated from the following equation.

$$\log P_1 = \frac{-10,454}{T_1} + 8.706$$

For example, the heating is given advantageously at a temperature of about 1500°C under normal pressure and of about 1200°C under a reduced pressure of about 50 mmHg. If the briquets are heated at the temperature satisfying the conditions just described, then the reaction leading to the formation of calcium-silicon alloy is accelerated, the formed calcium-silicon alloy is obtained in a molten state, the briquets consequently acquire hardness enough to withstand disintegration, the thermal conductivity is enriched, the magnesium oxide and the reducing agent in the briquets are brought into a state of intimate contact and conditions highly advantageous for the reducing reaction in the subsequent step are brought about. The briquets are subsequently subjected to solid-phase reduction in the following step. If, in this case, they are exposed to a temperature exceeding the melting point of the calcium-silicon alloy contained therein, or even after they have thoroughly released magnesium vapor, the briquets themselves are retained fast by the magnesium oxide or the high melting dicalcium silicate resulting from the reduction and, therefore, are kept from being disintegrated.

Now a description will be given of the reduction to which the briquets containing the calcium-silicon alloy are subjected. The reaction conditions (temperature and pressure) for this reduction can be selected in accordance with the vapor pressure of magnesium and the reaction velocity. Specifically, the heating is re+