UNITED STATES PATENT OFFICE.

WILLIAM M. GROSVENOR, OF RIDGEWOOD, NEW JERSEY. 

PROCESS FOR OBTAINING ALKALI-EARTH METALS.

1,239,178. 

Patented Sept. 4, 1917. 

Application filed February 3, 1916. Serial No. 76,017.

To all whom it may concern:

Be it known that I, WILLIAM M. GROSVENOR, a citizen of the United States, resident of Ridgewood, county of Bergen, State of New Jersey, have invented certain new and useful Improvements in Processes for Obtaining Alkali-Earth Metals, of which the following is a specification.

My invention relates to processes for obtaining alkali earth metals and is especially and particularly adapted to the obtaining of metallic magnesium.

One object of the invention is to provide a simple, cheap and efficient process by which such metals may be obtained in solid form, with great ease and rapidity. A further object of the invention is to provide a process by which such metals and particularly magnesium may be obtained in pure form by a simple and cheap method.

Further features and advantages of the invention will more clearly appear from the detailed description given below, taken in connection with the accompanying sheet of drawings, which forms a part of this specification and in which Figure 1 is a section through an apparatus in which my process in one form may be carried out, and Fig. 2 is a vertical section of a larger apparatus in which my process in one form may be carried out, both figures being somewhat diagrammatic.

In order to enable those skilled in the art to carry out and practice my improved process, I will describe in some detail one method for obtaining pure metallic magnesium, according to my invention, it being understood that the process may be widely varied and other metals obtained by my process in its broader aspects, all of which will be clearly understood by those skilled in the art. Consequently, I do not desire to be limited to the details herein described, but desire to cover all modifications which, as a matter of language, fall within the scope of the appended claims.

Carrying out the invention in the preferred form for obtaining of metallic magnesium, I take magnesium containing about 90% Si. The charge may have approximately the following formula:

$$2\text{MgO} + \text{CaO} (\text{in the calcined dolomite}) + \text{MgO(added as calcined magnesite)} + \text{Si} (\text{as 90% ferro-silicon}).$$

On heating to about 1350°C to 1550°C, this reacts to liberate magnesium vapor when the formula may become:

$$\text{MgO.CaO.SiO}_2 + 2\text{Mg}.$$ 

The charge should be finely ground and thoroughly mixed and is then given a prolonged heating, nearly to the temperature at which the magnesium vapor will be liberated, in a current of inert gas, to completely remove all volatile impurities therefrom that might be liberated in gaseous form when the temperature is raised sufficiently to liberate magnesium vapor. After these impurities have been removed by the current of inert gas, the temperature is raised to about 1600°C or between 1300°C and 1800°C, to liberate the magnesium vapor. The temperature is restrained to a point not far above the temperature at which magnesium vapor is liberated, in order to avoid volatilization of more refractory impurities. The uncontaminated, pure magnesium vapor is then condensed in an inert atmosphere to produce pure metallic magnesium. The excess of magnesium oxide, preferably containing some CaO, is added to the charge in order to make the same somewhat more basic, so that the temperature of fusion or melting of the charge is raised to a point above the reaction temperature at which magnesium vapor is liberated. The temperature to which the charge is originally raised for the purpose of eliminating volatile impurities may be about 1100°C, and the temperature should preferably be maintained about this point while the inert gas is passed through the charge to conduct away the volatile impurities.

Referring to Fig. 1 of the drawings, 1 represents a suitable iron tube surrounded throughout a portion of its length by an electric furnace 2. The furnace 2 consists of a series of carbon disks 3, through which the tube 1 passes. At each end of the pile of disks 3 there is a contacting plate 4, to which electrical conductors may be connected for the purpose of sending current through the carbon pile 3. At each end
there is provided a ring 5, insulated from the end member 4 by insulating ring 6, the rings 5 being connected together by rods 7, having thumb nuts 8, by means of which the pressure with which the carbon disks are pressed together may be varied, in order to vary the resistance of the carbon pile. By varying the current therethrough, and the heat liberated therein, the temperature within the tube 1 surrounded by the electric furnace may be varied. The charge of magnesium containing material is indicated at 9, in that part of the tube surrounded by the furnace 2. The left hand end of the tube 1 is provided with a cap 10 into which extends a small pipe 11, by means of which hydrogen or other inert gas may be conducted into the tube 1 and through the charge 9. At the other end the tube 1 has connected to it another tube or extension 12, having on its right hand end a cap 13, into which extends a small pipe 14, out of which the hydrogen or other inert gas and volatilized impurities may escape. The charge 9 being placed in the tube as indicated, current is turned on and the temperature raised to about 1100°C, hydrogen gas being passed into the tube 1 by means of the pipe 11. This current of inert gas forces the air and the impurities volatilized at this temperature out of the apparatus into or through the extension 12 and pipe 14. After all such impurities have been driven off, as shown by experience, another clean pipe 12 may be attached if necessary, and the temperature is raised to about 1600°C, whereupon magnesium vapor is expelled from the charge, and being carried along by the inert gas, will be condensed in the cool pipe 14 and extension 12. The inert hydrogen gas will, however, continue to flow from the pipe 14 and may be burned at its end. After sufficient time has been given for the magnesium vapor to be expelled and condensed in part 12, the cap 13 may be removed, and the condensed metallic magnesium removed therefrom. If desired, the whole extension 12 may be removed from the tube 1, to facilitate this operation. It will be understood also that the electric furnace may be inclosed by any suitable heat insulating material, in order to increase the efficiency of the apparatus.

Obviously other inert atmospheres may be provided, such as partial or nearly complete evacuation, to produce a substantially inert atmosphere, but I prefer the use of hydrogen, because of its low cost and the fact that its use does not entail the structural difficulties of a substantial vacuum.

Referring to the apparatus shown in Fig. 9, there is there shown a container 20, having a top wall 21, a bottom wall 22, and suitable side walls, all preferably formed of magnesite brick. The cross-section of the container may be substantially rectangular. The end walls of the container consist of hollow iron members 23, preferably inclined to the vertical, as shown, and provided with extending points or ribs 24. The end walls 23 have suitably connected thereto electrical conductors 25, so that the end walls 23 are adapted to act as electrodes, by which alternating electric current may be passed through the charge 26, placed in the container 20. That is, the charge 26 is heated by means of an electrical current, passing through the charge, the charge acting as a conductor for the current between the electrodes so that the charge acts as a chemically reacting resistance heater. The temperature is regulated by determining and varying the amount of current passing through the charge. In order that the end walls 23 may not become unduly heated, there are provided cooling fluid pipes 27, 28, extending thereinto, so that a circulation of cooling fluid may be had within the hollow end walls 23, for the purpose of keeping them cool. Surrounding the chamber 20 is a box-like inclosure 29 of heat and electric insulating material and made airtight. Extending into the top of the box-like structure 29 is a pipe 30, by means of which inert gas, such as hydrogen, may be delivered to the container. For this purpose the top and side walls are made porous or with sufficient apertures so that the hydrogen will freely enter into the container 20. Built up in the center of the container 20 is a cylindrical duct 31, built of magnesite brick, with spaces or apertures between the brick, so that any gases liberated from the charge may freely enter into the duct 31 and pass to the iron tubular condenser 32, having a cap 34 clearing its lower end and from which tube extends a small pipe 35, through which the gases may escape.

In order that the charge 26 may be made conducting, the same may be heated in any suitable manner, by the external application of heat, or a small current may be started through the charge in any suitable manner, sufficient to gradually heat up the charge until the charge becomes substantially wholly conducting. The inert gas delivered by the pipe 30 circulates freely throughout the surrounding box-like structure 29 and also throughout the container 20, so that all air, as well as volatilized impurities are carried away by the current of gas through the condenser 32 and pipe 35. After such impurities have been completely removed, the temperature is raised by increasing the current through the charge, until the temperature is approximately 1600°C, and magnesium vapor is liberated and is carried with the current of gas into the condenser 32, where it is condensed into metallic magnesium. As in the case of Fig. 1.
after the impurities have been removed, the hydrogen gas escaping from pipe 35 may be burned at the end of the pipe. The points or projecting ribs 24 materially aid in starting the current through the charge 26 but are not essential to the invention in its broader aspects. For example, suitable silicon electrodes of other forms may be used and the whole mass reduced to a fluid condition after the impurities have been volatilized, and during or after the liberation of the magnesium.

The exhausted charge may be removed from the container 30 by any suitable method, as either by digging it out or providing false bottoms within the container, by means of which the charge may be lifted out. Or, if preferred, the temperature may be raised to about 1800° C., (the charge made to contain a lesser excess of basic material) in order to fuse the residue and remove it in any suitable manner as a liquid. Obviously other materials than the silicon in ferro-silicon may be used, such, for instance, as aluminum or titanium, and I prefer to use a non-carboniferous reducing agent, although any suitable reducing agent may be used, but because of its cheapness and ease of manufacture, I prefer to use ferro-silicon.

What I claim as new and desire to secure by Letters Patent is:

1. The improved process of obtaining metallic magnesium which consists in prolonged heating of magnesium oxide containing material nearly to the temperature at which magnesium vapor would be liberated, in a current of inert hydrogen gas to remove volatile impurities therefrom and then heating the material in the presence of a reducing agent, sufficiently to cause magnesium vapor to be liberated but restraining the temperature to a point not far above the temperature at which metallic magnesium is liberated to avoid volatilization of more refractory impurities.

2. The improved process of obtaining metallic magnesium which consists in prolonged heating of magnesium oxide containing material nearly to the temperature at which magnesium vapor would be liberated, in a current of inert gas to remove volatile impurities therefrom and then heating the material in the presence of a reducing agent, sufficiently to cause magnesium vapor to be liberated.

3. The improved process of obtaining metallic magnesium which consists in heating magnesium oxide containing material with a reducing agent nearly to the temperature at which magnesium vapor will be liberated, in an inert atmosphere to remove volatile impurities therefrom, the material being sufficiently basic so that the melting point of the material is raised to a temperature above that at which the magnesium vapor is liberated, and then raising the temperature sufficiently to liberate magnesium vapor without melting the material, and condensing the liberated magnesium vapor while restraining the temperature of the material sufficiently to avoid volatilization of more refractory impurities.

4. The improved process of obtaining metallic magnesium which consists in heating magnesium oxide containing material with a suitable reducing agent nearly to the temperature at which magnesium vapor will be liberated to remove volatile impurities therefrom, the material being sufficiently basic so that the melting point of the material is raised to a temperature above that at which the magnesium vapor is liberated, and then raising the temperature sufficiently to liberate magnesium vapor.

5. The improved process of obtaining metallic magnesium which consists in heating magnesium oxide containing material in an inert atmosphere without substantially liberating magnesium vapor therefrom, to remove volatile impurities from the material and then heating the material in the presence of a suitable reducing agent of the material to liberate magnesium vapor and condensing said vapor to produce metallic magnesium.

6. The improved process of obtaining alkali earth metals which consists in heating to at least 700° F. alkali earth metal compound containing material in the presence of a suitable reducing agent at a point below the temperature at which vapor of the alkali earth metal will be liberated, to remove volatile impurities from the material and then raising the temperature of the material to cause vapor of the alkali earth metal to be liberated and condensing said vapor to obtain the alkali earth metal in metallic form in an inert atmosphere.

7. The improved process of obtaining alkali earth metals which consists in heating alkali earth metal compound containing material at a point below the temperature at which vapor of the alkali earth metal would be liberated, to remove volatile impurities from the material and then raising the temperature of the material and heating it in the presence of a suitable reducing agent without melting the same to cause vapor of the alkali earth metal to be liberated and condensing said vapor to obtain the alkali earth metal in metallic form.

8. The improved process of obtaining alkali earth metals which consists in prolonged heating of alkali earth metal compound containing material in the presence of a non-carboniferous metalloid reducing agent, such as ferro-silicon, at a point below the temperature at which vapor of the alkali earth metal will be liberated, to remove
volatile impurities from the material, the material being sufficiently basic so that it will not melt at the temperature at which vapor of the alkali earth metal is liberated, and then raising the temperature of the material to cause vapor of the alkali earth metal to be liberated and condensing said vapor to obtain the alkali earth metal in metallic form.

9. The improved process of obtaining alkali earth metals which consists in prolonged heating of alkali earth metal compound containing material in a current of inert gas nearly to the temperature at which vapor of the alkali earth metal will be liberated to remove volatile impurities from the material, and then raising the temperature of the material and reducing the compound to cause vapor of the alkali earth metal to be liberated and condensing said vapor to obtain the alkali earth metal in metallic form.

10. The improved process of obtaining metallic magnesium which consists in heating magnesium oxide containing material in an inert atmosphere of hydrogen without substantially liberating magnesium vapor therefrom, to remove volatile impurities from the material and then heating the material in the presence of a reducing agent between 1300° C. and 1600° C. to liberate magnesium vapor and condensing said vapor to produce metallic magnesium.

11. The improved process of obtaining alkali earth metals which consists in prolonged heating of alkali earth metal compound containing material with a suitable reducing agent nearly to the temperature at which vapor of the alkali earth metal will be liberated to remove volatile impurities from the material, and then raising the temperature of the material to a point between 1300° C. and 1600° C. to cause vapor of the alkali earth metal to be liberated and condensing said vapor to obtain the alkali earth metal in metallic form.

12. The improved process of obtaining metallic magnesium which consists in heating magnesium oxide containing material in the presence of a reducing agent in a current of inert gas nearly to the temperature at which magnesium vapor will be liberated to completely remove all volatile impurities therefrom that might be liberated in gaseous form when the temperature is raised sufficiently to liberate magnesium vapor, and then increasing the temperature sufficiently to liberate magnesium vapor without volatilizing more refractory impurities.

13. The improved process of obtaining alkali earth metals which consists in prolonged heating of alkali earth metal compound containing material with a suitable reducing agent in a current of inert gas nearly to the temperature at which vapor of the alkali earth metal will be liberated to completely remove all volatile impurities therefrom that might be liberated in gaseous form when the temperature is raised sufficiently to liberate vapor of the alkali earth metal, and then increasing the temperature sufficiently to liberate vapor of the alkali earth metal without volatilizing more refractory impurities and then condensing the alkali earth metal vapor in an inert atmosphere.

14. The improved process of obtaining metallic magnesium which consists in heating and reducing magnesium oxide containing material at a temperature between 1300° C. and 1800° C. to produce pure magnesium vapor and condensing said vapor in an inert atmosphere to produce pure metallic magnesium.

15. The improved process of obtaining metallic magnesium which consists in heating and reducing a magnesium compound containing material in an inert atmosphere under conditions to produce pure magnesium vapor and condensing said vapor in an inert atmosphere to produce pure metallic magnesium.

16. The improved process of obtaining metallic magnesium which consists in prolonged heating of magnesium oxide containing material nearly to the temperature at which magnesium vapor would be liberated to remove volatile impurities therefrom and then heating the material in the presence of a reducing agent sufficiently to cause magnesium vapor to be liberated but restraining the temperature to a point not far above the temperature at which metallic magnesium is liberated to avoid volatilization of more refractory impurities.

17. The improved process of obtaining metallic magnesium which consists in prolonged heating of magnesium oxide containing material in the presence of a suitable reducing agent nearly to the temperature at which magnesium vapor will be liberated to remove volatile impurities therefrom and then raising the temperature sufficiently to cause magnesium vapor to be liberated.

18. The improved process of obtaining metallic magnesium which consists in prolonged heating of magnesium oxide containing material nearly to the temperature at which magnesium vapor would be liberated to remove volatile impurities therefrom and then heating the material in the presence of a reducing agent sufficiently to cause magnesium vapor to be liberated and condensing the liberated magnesium vapor in an inert atmosphere.

19. An apparatus of the class described having in combination a container of magnesite brick for the charge, electrodes disposed oppositely in said container, an air tight inclosure for said container, means for
admitting an inert gas to said inclosure and container and a condenser connected to said container, said condenser being provided with an exit for said inert gas the charge acting as a chemically reacting heating resistance between the electrodes.

20. An apparatus of the class described having in combination a container, electrodes disposed oppositely in said container a chemically reacting heating resistance forming a path for the current between said electrodes, an air tight inclosure for said container, means for admitting an inert gas to said inclosure and container and a condenser connected to said container.

21. An apparatus of the class described having in combination a container for the charge, electrodes disposed oppositely in said container, an air tight inclosure for said container, means for admitting an inert gas to said inclosure and container and a condenser connected to said container, and a porous duct extending into said charge for leading the gases or vapors to the condenser.

In testimony whereof, I have signed my name to this specification.

WILLIAM M. GROSVENOR.