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[54] **PROCESS FOR THE METALLOTHERMIC PRODUCTION OF MAGNESIUM**

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[52] **U.S. Cl.** **75/67**

[51] **Int. Cl.** **C22b 45/00**

[58] **Field of Search** 75/67

[56] **References Cited**

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[57] **ABSTRACT**

A method of producing magnesium by the reduction of magnesium oxide by means of a metallic reducing agent, in the presence of a molten oxidic slag, wherein the system contains an inert gas to obviate at least in part the need of a high vacuum.

12 Claims, No Drawings

PROCESS FOR THE METALLOTHERMIC PRODUCTION OF MAGNESIUM

BACKGROUND AND GENERAL DESCRIPTION OF THE INVENTION

This application is a continuation-in-part of my copending application, Ser. No. 648,856, filed June 26, 1967 now U.S. Pat. No. 3,579,326, issued May 18, 1971. This application is a parent of continuation-in-part applications Ser. Nos. 26,118 and 26,116 filed Apr. 6, 1970; and Nos. 143,866 and 144,321 filed May 17, 1971.

This invention is concerned with the production of metallic magnesium by the metallothermic reduction of magnesium oxide at elevated temperature, and it relates to an improved process wherein magnesium oxide, usually in the form of calcined dolomite or calcined magnesite or mixtures thereof, is caused to react with a metallic reducing agent, such as silicon, aluminum, calcium or mixtures or alloys thereof, in the presence of a molten slag bath in a furnace at temperatures in excess of 1300°C., to release magnesium vapor which may be condensed and collected. In particular, the process of this invention operates in the presence of an inert gas at a partial pressure of at least one-tenth atmosphere.

For reasons which will be discussed, the commercial process of this type, known as the Magnetherm process, is operated under very high vacuum. It is the purpose of this invention to provide means whereby operation under high vacuum may be avoided, and the process operated more nearly at atmospheric pressure or at least under lower vacuum, thereby improving the technology and economics of the process.

The equipment in which such a process has been carried out comprises in sequence: feed bins in which the raw materials are stored and from which they are fed to the furnace through ducts or tubes; the furnace proper in which the reducing reaction takes place; a throat or duct through which magnesium vapor released in the reaction zone passes; a condenser in which the magnesium vapor is condensed to molten metal; and a pot or crucible attached to the condenser in which the molten magnesium is collected.

In the Magnetherm process a vacuum system removes such gasses as may appear in the system, and maintains a high vacuum, usually corresponding to an absolute pressure of less than about one-twentieth atmosphere. The operation of such an extensive system under very high vacuum at elevated temperatures involves design, engineering, construction and operating problems, the alleviation of which is the object of the present invention.

Magnesium vapor is the only gaseous product of the desired reaction—the other products being molten slag and spent alloy—and this vapor is condensed to molten metal as rapidly as it is formed. The absolute pressure in the Magnetherm system is essentially that corresponding to the vapor pressure of magnesium at or somewhat above its melting point, namely less than about one-twentieth atmosphere. Thus, in effect, magnesium formed in the reaction zone is distilled from the furnace under very high vacuum, condensed, and collected in the crucible as molten (or solid) metal.

In such an operation it is necessary to remove the molten products from the system periodically; tapping the furnace under high vacuum to remove molten slag and spent reductant is impractical, and it is difficult to remove molten magnesium from the crucible under high vacuum. The procedure used in the Magnetherm process is periodically to stop the reaction and then to break the vacuum, thus permitting the furnace to be tapped and the crucible removed. As soon as the furnace is plugged and the crucible replaced by a fresh one, vacuum is once more applied, and the operation is started again.

DETAILED DESCRIPTION OF THE INVENTION

In general terms, the present invention may be characterized as the reduction of magnesium oxide by means of a metallic reducing agent in the presence of a molten oxidic slag at a temperature above 1300°C. wherein the magnesium vapor is evolved and condensed in an atmosphere at an absolute pressure of at least one-tenth atmosphere and comprising an inert gas at a partial pressure of at least about one-tenth atmosphere.

Thus, the present invention provides a process of the Magnetherm type which produces magnesium vapor under a relatively high absolute pressure, due in part at least to the presence of an inert gas. This added pressure may be utilized to decrease or eliminate the pressure differential between the interior of the system and the atmosphere. As employed herein, the term "high vacuum" refers to an absolute pressure of less than one-twentieth atmosphere, and a "relatively high pressure" is one-tenth atmosphere or higher.

Heretofore it has been supposed that removal of magnesium vapor from the reaction zone by distillation under high vacuum is necessary in order to promote the reducing reaction:

$$2MgO(1) + Si(1) \longrightarrow SiO_2(1) + 2Mg(\uparrow);$$

thus driving the reaction from left to right, and that a relatively high absolute pressure in the system (i.e., above one-tenth atmosphere) would be detrimental; hence the use of a very high vacuum. First, an increase in magnesium partial pressure would tend to reverse the reaction which produces the magnesium in the reaction zone. Second, the presence of a higher total pressure, even at the same magnesium partial pressure, could inhibit the transfer of magnesium vapor though the duct and into the condenser, as well as retard the reaction. However, in accordance with the present invention, an absolute pressure of up to at least about 1 atmosphere, including the partial pressure of both magnesium and an inert gas, will not inhibit the reaction to a serious extent; and under normal conditions gaseous diffusion alone will provide a mass transfer rate of magnesium vapor from furnace to condenser sufficient to keep pace with the rate of production in the furnace. Thus it becomes possible to operate the system under atmospheric pressure or thereabouts, or in any event at relatively high absolute pressure, i.e., above one-tenth atmosphere.

In accordance with the present invention, magnesium is produced and vaporized in the presence of an inert gas at a partial pressure of at least one-tenth atmosphere. The total pressure of the system, including the partial pressure of both the magnesium and the inert gas, is at least one-tenth atmosphere, and preferably about ½ to 1 atmosphere. The partial pressure of the magnesium in the furnace depends, of course, upon other conditions, primarily the temperature of the slag bath, but also the concentration of magnesium oxide, the composition of the reducing agent, the temperature of the condenser and the production rate. There is of necessity a pressure differential of the magnesium vapor between the furnace and the condenser to provide the mass-transfer driving force for the diffusing magnesium. Ordinarily, the magnesium partial pressure is about one-twentieth atmosphere, and preferably no more than one-half atmosphere. The partial pressure of the inert gas also is dependent on other factors, but is at least one-tenth atmosphere, and preferably between about ½ and 1 atmosphere. Ordinarily, the partial pressure of the inert gas need not be higher than 1 atmosphere (or slightly less) in order that the absolute pressure of the system be about 1 atmosphere. But, if desired, the absolute pressure may be higher, and the partial pressure of the inert gas may be correspondingly higher. It may be advantageous to increase the absolute pressure of the system above 1 atmosphere, for example, in order to assist the periodic removal of spent products or magnesium from the system. It appears that there is no benefit in having the inert gas partial pressure, or the absolute pressure of the system, higher than about 2–5 atmospheres.

As employed herein, the term "inert gas" includes those gaseous materials that are non-reactive with the components of the system under the conditions of operation. Because of the high chemical activity of magnesium at elevated tempera-

ture, few gases can be considered inert in the present process. Suitable inert gases include the literally inert gases, such as helium, neon, argon and the like. Another non-reactive gas is hydrogen, which is in certain respects desirable. Hydrogen is cheap and easily available, it provides excellent characteristics for heat transfer in the condenser, and it provides a relatively high specific rate of diffusion. If for some reason air leaks into the system, its oxygen should react with magnesium in preference to the hydrogen. If the hydrogen leaks out of the system, it should either burn or otherwise be dissipated innocuously. Any other gas with equivalent inertness may be used in this invention.

The magnesium oxide reactant may comprise magnesia, usually derived from magnesite by calcination, or calcined dolomite, an equimolar combination of magnesium oxide and calcium oxide, or mixtures of both. In order to enhance the reaction the magnesium oxide content of the system should be maintained relatively high, above 5 percent and preferably between about 10 and 20 percent, measured as a fraction of the oxidic slag.

The metallic reducing agent may be silicon, aluminum, aluminum-silicon, ferrosilicon-aluminum, calcium-silicon, calcium-aluminum-silicon or the like. Preferably an aluminum-silicon alloy, containing silicon and aluminum in a ratio of at least 0.8:1, is employed. High utilization of the silicon is possible with such alloys. Apparently, the presence of aluminum in close physical association with the silicon stimulates the reductant synergistically, and a major fraction of the silicon may be utilized to reduce the magnesium oxide. Scrap aluminum may be used, and it may be added to provide part of the reducing agent. As employed herein the terms "aluminum", "silicon" and "aluminum-silicon alloy" include those reductants which, when added to the molten slag in the reaction zone of a reducing furnace, as herein described, provide metallic aluminum, silicon or both.

For economic reasons, in part, a ferrosilicon alloy is preferred, for example a ferrosilicon-aluminum alloy containing about 0–25 percent iron, 40–65 percent silicon and 25–50 percent aluminum, particularly in view of the ready availability of such aluminum-silicon alloys. Such alloys can be manufactured by electric furnace smelting procedures, which are well known. As the aluminum content of the alloy increases, a small proportion of iron is desirable or, at times, even necessary in order to prevent excessive volatilization of aluminum and silicon from the furnace. It is generally considered that the aluminum content of these alloys is for practical reasons limited to about 60 percent maximum. In such cases the iron content is generally greater than about 5 percent. On the other hand, for maximum utilization of the silicon content, it is desirable to have a relatively low iron content in the reductant of this invention. But this desideratum must be balanced against the favorable effect of iron content on the cost of producing the reductant alloy, as mentioned above. An iron content of about 10 percent appears to be satisfactory considering these factors, but it may be higher or lower without departing from the spirit of the invention, for example in the range of 0 to 25 percent. As is well known, titanium and other metallic oxides are sometimes present in the raw materials used for the production of an aluminum-silicon alloy, and the corresponding metal is therefore sometimes present in the alloy produced. The presence of such "tramp" metals does not interfere with the operation of the process of this invention, and may be tolerated or remedied by suitable metallurgical procedures.

The oxidic slag generally contains a mixture of calcium, aluminum and silicon oxides, sometimes called a calcium-aluminum-silicate or lime-alumina-silica slag, in combination with the magnesium oxide reactant. One or more of these oxides may of course be a product of the reaction, depending on the reductant used, which could, along with the consumption of magnesium oxide, vary the slag composition as the reaction proceeds. The composition of the slag in any case is about 10–60 percent calcium oxide, 10–35 percent aluminum oxide, 20–50 percent silica and 5–25 percent magnesium oxide. A typical slag might contain 50 percent calcium oxide, 20 percent aluminum oxide, 25 percent silica and 5 percent magnesium oxide. A preferred slag composition is about 25–30 percent silica, 20–25 percent alumina, 35–40 percent calcium oxide and 10–15 percent magnesium oxide; another is about 30–45 percent silica, 25–30 percent alumina, 10–20 percent calcium oxide and 10–20 percent magnesium oxide. The temperature of the slag, and hence of the system, depends primarily on the slag composition (i.e., it must be molten), but the temperature is usually at least 1300°C., and preferably about 1400°–1700°C.

In the process of the present invention it is highly desirable to maintain in the reaction zone a temperature of at least about 1400°C. to promote good reaction conditions, but temperatures higher than about 1700°C. are undesirable because they create difficult engineering and operating problems. It is therefore desirable to employ a slag whose melting point is not higher than about 1600°C. in order that enough superheat may be applied to impart sufficient fluidity to the slag without the necessity of excessively high temperature. Thus, a temperature of about 1400°–1700°C. in the reaction zone is preferred, although in certain instances higher or lower temperatures are suitable and may be desired.

On the other hand slags of relatively high viscosity can be used in the present process because there is in the furnace no bed of solid material through which the slag must find its way in order to reach the tap hole for removal from the furnace. Thus the problem of slag viscosity is not as great as it is in most metallurgical processes, but it is still a factor requiring attention.

In general, the composition of the slag is determined in the present process by the ratio of aluminum to silicon fed as the reducing agent; the degree of utilization of silicon as reductant, which for reasons of economy should be as high as feasible; the relative proportions of magnesium oxide fed as magnesia and as dolomitic lime; and the amount of alumina (if any) as a flux.

Ordinarily, diffusion of magnesium vapor alone is sufficient to provide for the mass transfer from the reactor to the condenser. However, if desired, a stream of the inert gas may be introduced into the furnace and fed through the condenser, in order to augment the magnesium flow to the condenser, in which case a recycle system may be utilized to recover the inert gas. A recycle system may be desired in any case to recover inert gas, especially if a vacuum system is employed.

In the operation of a process such as has been described, small amounts of impurities in the raw materials fed to the system (e.g., residual CO_2 and H_2O in the oxidic portion of the charge, and air trapped with the raw materials in the feed hoppers) may find their way into the furnace and produce reactive gases, such as CO and N_2, which should be vented from the system. These gases may be removed as required by bleeding off the inert gas, in which they will be present as impurities, in order to prevent the buildup of reactive gas on the one hand, or, alternatively, to prevent an increase of pressure.

The operation of the present process under relatively high absolute pressure significantly decreases the leakage of air into the system. This decrease is advantageous, since the presence of air results in the reaction of oxygen and nitrogen with the magnesium product not only to decrease yield but also to form accretions of solid matter on the system walls. In particular the decrease of solids deposited on the heat transfer surfaces substantially increases the condenser efficiency and extends the period between shutdowns. Moreover, a high absolute pressure, particularly as atmospheric pressure is approached, makes it possible to operate the process as a continuous or semicontinuous process, with attendant benefits, such as facilitating removal of spent slag and magnesium product. Further, even if a batch process is used, the need for a hermetically sealed reaction-condensation system may be eliminated—and problems, such as vacuum breaking, may be avoided—completely, or at least in part.

I claim:

1. A metallothermic process for the production of magnesium in a reaction-condensation system having a reducing furnace reaction zone and a condenser, which comprises charging a metallic reducing agent and magnesium oxide to the reaction zone, containing a molten oxidic slag bath at a temperature of at least about 1300°C., evolving magnesium vapor from the reaction zone to the condenser and condensing and recovering the magnesium as a product, wherein said evolving and condensing is done in the presence of an inert gas at a partial pressure of between about 1/10 and 5 atmospheres in said reaction-condensation system.

2. The metallothermic process of claim 1, wherein the inert gas is selected from the group consisting of helium, neon, argon and hydrogen.

3. The metallothermic process of claim 1, wherein the molten oxidic slag comprises 10–60 percent calcium oxide, 10–35 percent aluminum oxide, 20–50 percent silica and 5–25 percent magnesium oxide.

4. The metallothermic process of claim 1, wherein the metallic reducing agent is selected from the group consisting of aluminum, silicon and aluminum-silicon alloys.

5. The metallothermic process of claim 1, wherein the absolute pressure of the reaction-condensation system is about ½ to 1 atmosphere.

6. The metallothermic process of claim 1, wherein the absolute pressure of the reaction-condensation system is about 1 atmosphere.

7. The metallothermic process of claim 1, wherein the partial pressure of the inert gas is about ½ to 1 atmosphere.

8. A metallothermic process for the production of magnesium in a reaction-condensation system including a reducing furnace reaction zone and a condenser, which comprises charging a reducing agent, selected from the group consisting of aluminum, silicon and aluminum-silicon alloys, and an oxidant comprising magnesium oxide to the reaction zone, containing a molten oxidic slag comprising about 10–60 percent calcium oxide, 10–35 percent aluminum oxide, 20–50 percent silica and 5–25 percent magnesium oxide at a temperature of about 1400° to 1700°C., and, in an atmosphere containing an inert gas at a partial pressure of between about 1/10 and 5 atmospheres, evolving magnesium vapor from the reaction zone to the condenser and condensing the magnesium.

9. The metallothermic process of claim 8, wherein the inert gas is selected from the group consisting of helium, neon, argon and hydrogen.

10. The metallothermic process of claim 8, wherein the absolute pressure of the reaction-condensation system is about ½ to 1 atmosphere.

11. The metallothermic process of claim 8, wherein the absolute pressure of the reaction-condensation system is about 1 atmosphere.

12. The metallothermic process of claim 8, wherein the partial pressure of the inert gas is about ½ to 1 atmosphere.

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