Jan. 1, 1974 J. M. AVERY 3,782,922

ALUMINOTHERMIC PRODUCTION OF MAGNESIUM AND AN OXIDIC SLAG CONTAINING RECOVERABLE ALUMINA

Filed April 18, 1972

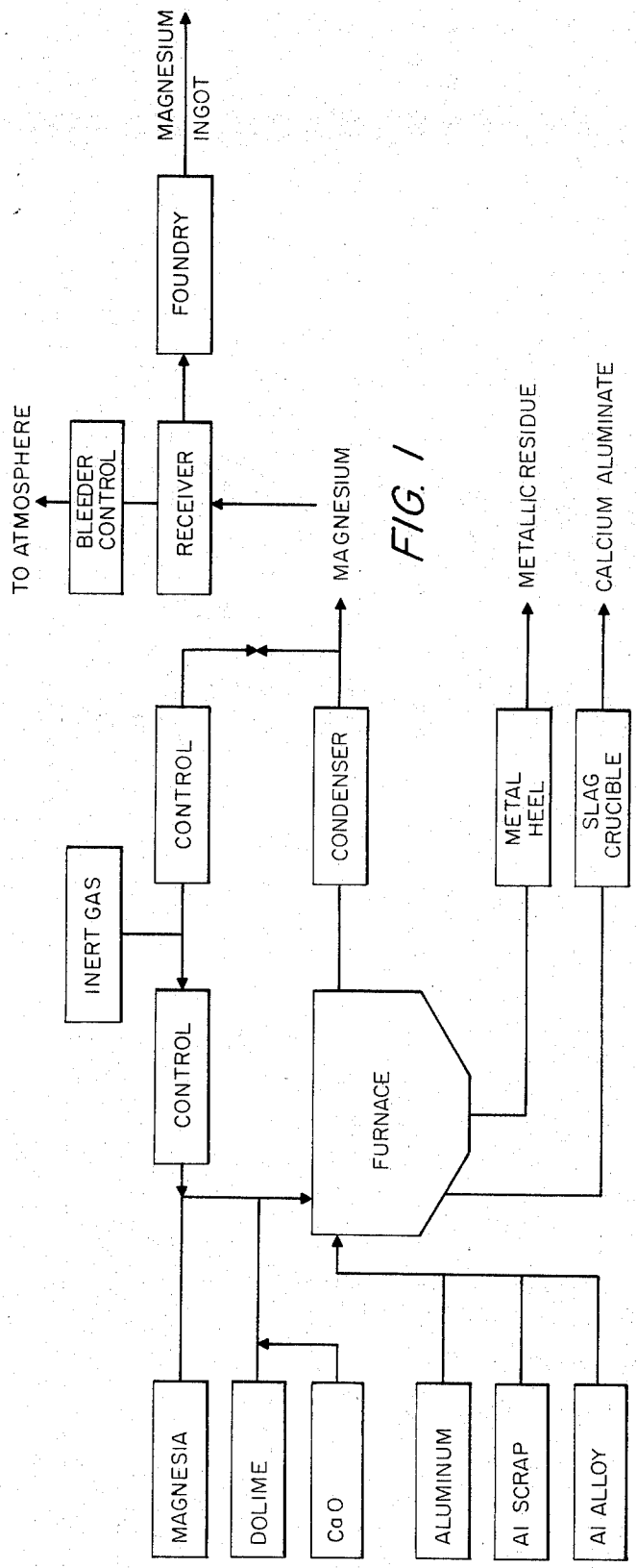


FIG. 1

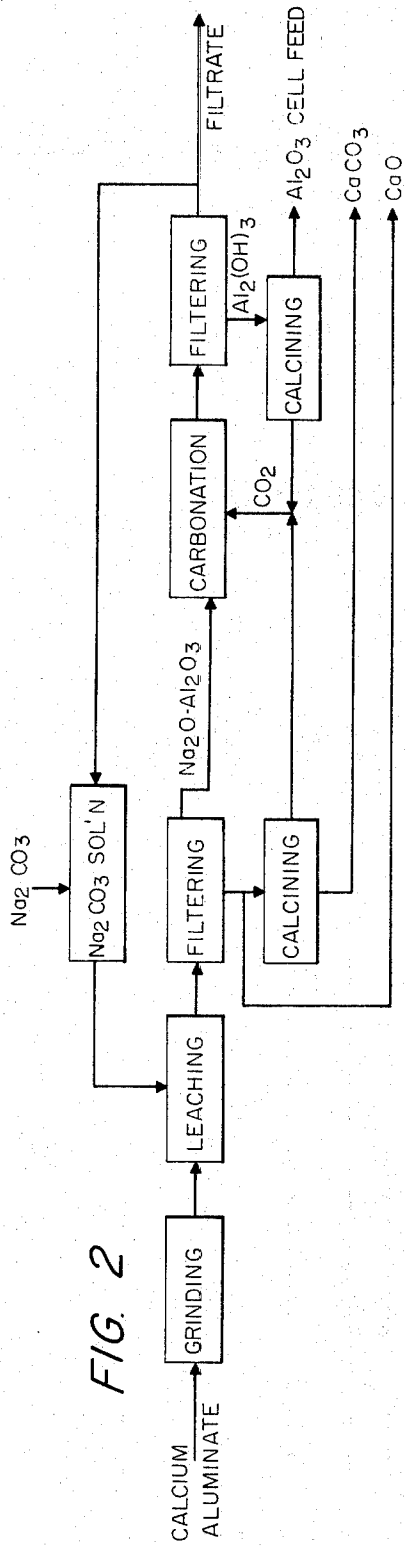


FIG. 2

United States Patent Office

3,782,922
Patented Jan. 1, 1974

3,782,922

ALUMINOTHERMIC PRODUCTION OF MAGNESIUM AND AN OXIDIC SLAG CONTAINING RECOVERABLE ALUMINA

Julian Miles Avery, 47 Old Orchard Road, Chestnut Hill, Mass. 02167

Continuation-in-part of applications Ser. No. 796,214, Feb. 3, 1969, now Patent No. 3,658,509, dated Apr. 25, 1972, Ser. No. 26,118, Apr. 6, 1970, Ser. No. 143,886 and Ser. No. 144,321, both May 17, 1971, all of which in turn are continuation-in-parts of application Ser. No. 648,856, June 26, 1967, now Patent No. 3,579,326, dated May 18, 1971. This application Apr. 18, 1972, Ser. No. 245,142

Int. Cl. C22b *45/00*

U.S. Cl. 75—67 14 Claims

ABSTRACT OF THE DISCLOSURE

An aluminothermic process for the production of magnesium by the reduction of magnesium oxide from a mixture of magnesium oxide and calcium oxide, by means of a metallic reducing agent comprising at least 85 percent aluminum, in the presence of a molten calcium-aluminate slag bath at a temperature of about 1300–1700° C. Magnesium evolves from the molten slag as a vapor. The process may be operated continuously and at atmospheric pressure. The molten slag residue is tapped periodically, when the MgO level is below 5 percent, and has a composition of 35–65 percent Al_2O_3, 35–55 percent CaO and 0–10 percent SiO_2 (by weight). The disclosure demonstrates how the ratio of magnesium oxide to calcium oxide in the charge and the quantity and composition of the metallic reducing agent are interrelated in such a way that (1) virtually all of both the reducing agent and magnesium oxide are consumed in the reducing reaction, and (2) the calcium-aluminate slag produced is of such a composition that pure alumina can be recovered from it with a very high yield.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of (1) Ser. No. 796,214, filed Feb. 3, 1969, patented Apr. 25, 1972, No. 3,658,509, directed to the use of inert gas in the vapor space above a molten oxidic slag bath for the metallothermic production of magnesium; (2) Ser. No. 26,118, filed Apr. 6, 1970, directed to the use of a substantially static atmosphere of inert gas in the vapor space above a molten slag for the metallothermic production of magnesium; (3) Ser. No. 143,886, filed May 17, 1971, directed to the metallothermic production of magnesium induced by a stream of inert gas in a system containing a molten oxidic slag; and (4) Ser. No. 144,321, filed May 17, 1971, directed to the metallothermic production of magnesium from a molten oxidic slag wherein hydrogen is used in the vapor space above the slag, all of the above applications were in turn continuation-in-parts of Ser. No. 648,856, filed June 26, 1967, now Pat. No. 3,579,326, issued May 18, 1971, directed to the reduction of magnesium oxide to magnesium with an aluminum-silicon alloy in the presence of an acidic molten oxide slag.

SUMMARY OF THE INVENTION

An aluminothermic process for the production of metallic magnesium from oxidic ores using a reducing agent consisting of metallic aluminum or one or more aluminum alloys containing at least 85 percent aluminum by weight, in the presence of a by-product, calcium-aluminate slag from which aluminum oxide can be readily recovered. General features of the process are:

(a) The reduction reaction is carried out in an internally heated electric furnace, at a temperature between about 1300° C. and 1700° C., preferably about 1500° C.

(b) Magnesium vaporized by the reaction is recovered in a condenser and collected in a crucible, preferably as molten magnesium.

(c) The entire system of furnace, condenser and crucible is preferably maintained at about atmospheric pressure. The magnesium may be evolved from the molten slag at a partial pressure of about atmospheric pressure and condensed by suitable procedures, or, alternatively, at a lower partial pressure in a system containing inert gas. Either alternative permits continuous or nearly continuous operation, since at atmospheric pressure molten slag and magnesium can readily be removed from the furnace and the crucible.

(d) The oxidic and metallic raw materials are so proportioned to produce a slag of such composition that the alumina contained in the molten slag will crystallize, as the slag cools, in the form predominately of soluble calcium aluminates, i.e. $CaO \cdot Al_2O_3$ (64.5% Al_2O_3) or $12CaO \cdot 7Al_2O_3$ (51.5% Al_2O_3), or both.

The formation of such a slag requires that the ratio in the oxide charge of MgO to CaO be about 1.1 to 2.3 by weight. If dolomite is used as the source of CaO for the process, the corresponding weight ratio of dolime to magnesia is about 1.2 to 3.8. Alternatively, magnesia (MgO) and lime (CaO) may be used.

It is within the scope of the present invention to produce such slags either by using low grade magnesia, e.g., siliceous magnesite, by using metallic silicon to supplement aluminum as the reducing agent, or by using an aluminum alloy containing some silicon.

However, the production of a silica-containing slag should not be a preferred form of the invention (because alumina recovery is higher without it), but it is an efficient modification to utilize cheap, low grade magnesite, or scrap aluminum containing silicon, or to employ when alumina recovery is not desired.

While extraction of Al_2O_3 from calcium-aluminate slags is not essential to the practice of the present invention, it is an important adjunct of the process. U.S.B.M. studies have shown that to achieve the purpose it is not necessary to produce a disintegrating slag containing silica. In fact, slags composed of the pure oxidic compounds $CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$, and presumably mixtures thereof, can be leached with nearly 100 percent efficiency with Na_2CO_3 solution (no free NaOH) at 70° C. in about 1 hour, with practically no residue except the $CaCO_3$ formed by the reaction of Na_2CO_3 to dissolve Al_2O_3 as sodium aluminate.

Carbonation to precipitate $Al(OH)_3$ from the solution regenerates the Na_2CO_3 and the solution may be recycled with whatever make-up Na_2CO_3 may be required due to losses.

Comparison of this extraction process with the usual commercial processes (Bayer and Pedersen) leads to the conclusion that it is simpler and cheaper to operate and requires less capital investment than either. A further advantage of the proposed low silica or silica-free slag

of the invention is that it makes possible the production of cell-grade Al_2O_3 without a separate desilication step, which is sometimes necessary when silicous bauxites are processed. Thus the Al_2O_3 content is more valuable per unit than the Al_2O_3 content of high grade bauxite used in the commercial Bayer process, and considerably more valuable than the Al_2O_3 content of low grade bauxites used for the Pedersen process. Moreover, it seems quite possible that the leaching operation can be carried out in an existing alumina plant, even though some of the equipment will be superfluous.

An important feature of the present process is that it can use as a reducing agent cheap aluminum scrap—either captive scrap from aluminum production plants or scrap purchased from aluminum fabricating plants. At once the question arises whether the use of such scrap might adversely affect the technology of the process or the quality of the magnesium metal produced, because of the alloying agents present in the many types of alloyed aluminum used for fabrication. A survey of the compositions of the usual alloys shows that the principal alloying metals used are magnesium, silicon, copper, manganese, chromium and zinc, in amounts generally less than 5 percent but up to 12 percent in at least one alloy.

Finally, there is the question of aluminum itself as an impurity in the magnesium product, since aluminum has a vapor pressure of about 10 mm. Hg at 1500° C. This means that magnesium produced by the present process will inevitably contain aluminum—how much depends upon the operating temperature. At 1400° C., for example, it would contain about 0.5 percent, at 1500° C. about 1.2 percent and at 1600° C., about 2 percent of aluminum. However, this is not a serious problem and may in fact be beneficial, because: (a) the principal use for magnesium today is to produce aluminum alloys for fabrication; and (b) a major portion of the magnesium used for fabricated magnesium products contains a substantial proportion of aluminum—generally from 3 to 9 percent. Thus the presence of a small amount of aluminum in the magnesium produced by the present process is not detrimental, especially if the magnesium operation is associated with the production of aluminum, which is likely to be the case because of the advantage of recovering Al_2O_3 from the slag produced, and the possibility of using captive scrap as the reducing agent.

From this point of view the process of the invention might be characterized in its preferred form by its overall results: the conversion of scrap aluminum into virgin magnesium coupled with the conversion of magnesium oxide into cell-feed alumina.

BACKGROUND OF THE INVENTION

There are two known commercial processes for the metallothermic production of magnesium; both are batch operations carried out under very high vacuum. Neither has been operated on a large scale comparable to the generally practiced production of magnesium by electrolysis of molten magnesium chloride.

The object of the present invention is to provide a metallothermic process which can compete successfully with the electrolytic process on either a large or a small scale. It is especially adapted for use by a company which manufactures and fabricates aluminum, because of the availability of captive scrap, facilities for recovering alumina from the slag, and a need for a high grade alumina for aluminum cell feed. But it can also be operated independently, particularly if based upon an adequate supply of scrap aluminum at low cost.

In one of the present commercial metallothermic processes*, known as the "Pidgeon Process," ferrosilicon (about 75 percent Si) and dolomite lime are charged into a battery of externally fired horizontal tubular retorts, and the magnesium is collected as a "crown" by condensation in an extension of the retort. Because the retorts cannot withstand very high temperatures, the reaction is necessarily a solid state reaction, and at a relatively slow rate. This process has high capital investment and operating cost, and is used only where the exceptionally high quality of the magnesium produced can command a premium price.

The other present commercial metallothermic process, known as the "Magnetherm Process," also uses dolomitic lime as the source of MgO and ferrosilicon (about 78 percent) as the reducing agent. The reduction is carried out at about 1500° C. in the presence of a molten calcium-aluminum-silicate slag, in an internally heated electric furnace. The ratio of slag to magnesium is very high—about 6 to 1, which creates a disposal problem unless it can be sold or used to produce cement, for which it has little value. The Al_2O_3 required to produce a slag of the desired composition, must be added to the furnace as either alumina or bauxite. The process is a batch operation, due to the necessity of cutting off power and breaking vacuum in order to tap slag halfway through the batch, and to tap slag and spent ferrosilicon and to remove the magnesium crucible at the end of the batch. Under very high vacuum, air leaks into the system, and magnesium is lost, not only by oxidation or nitridation, but also due to problems associated with the condenser and crucible, which must be removed, cleaned and replaced at the end of each batch.

The present invention provides a process which can be operated continuously at atmospheric pressure with high overall recovery of magnesium, which produces a co-product calcium-aluminate valuable as a source of alumina—both at low capital and production costs.

A so-called modified aluminothermic process, called the MC process (see Emley, supra, p. 50; British Pat. No. 922,300; Light Metals (February 1964), p. 44), has also been posed and briefly described. The process and its modifications, as described, have several disadvantages. The slag formed in one such process (see Brit. Pat. 922,-300), because it contains 15 percent MgO, cannot practically be used to recover Al_2O_3 as can the present slag.

Certain experiments relating to the reduction of magnesium oxide ores with aluminum are reported in Trans. Can. Inst. Min. Met., 1962, 65, pp. 221–224. The purpose of the experiments was to determine the vapor pressure of the magnesium product obtained by the reduction of magnesia, dolomite and olivine with aluminum. These studies conclude that the reaction product of the reduction of magnesia is magnesium aluminate, and that the reaction product of reduced dolomite is either

$$12CaO \cdot 7Al_2O_3$$

(below 1200° C.) or $3CaO \cdot Al_2O_3$ (above 1200° C.). Contrary to these results, I have found that it is possible to obtain at a temperature of about 1300–1700° C. a calcium-aluminate slag predominately containing

$$12CaO \cdot 7Al_2O_3,\ CaO \cdot Al_2O_3$$

or mixtures thereof. Alumina can be readily recovered from both of these oxide products, or mixtures thereof, whereas the product suggested in the reference,

$$3CaO \cdot Al_2O_3$$

is insoluble and does not permit the recovery of alumina therefrom.

The present invention offers numerous advantages over the above-mentioned metallothermic processes. First, virtually all of the aluminum reducing agent can be consumed in the primary reaction, thereby avoiding the necessity of recycling or disposal of considerable quantities of spent metal, such as iron alloys when ferrosilicon or ferro-aluminum is used. Second, the magnesium oxide charge, preferably a mixture of magnesia and cal-

*The various thermal reduction processes, including those detailed herein, are described with bibliography to pertinent patents and publications in Principles of Magnesium Technology, E. F. Emley, Pergamon Press (London, 1966), pp. 46–64; and a comparison is given between the electrolytic and metallothermic processes at pp. 65–67.

cined dolomite, can contain a desirably high ratio of MgO to CaO. Together, these advantages mean that the furnace capacity is much higher than with previous processes. Third, the aluminum reducing agent is far more reactive, and fourth, the molten slag can be fluid at a relatively low temperature; which advantages permit operation at relatively low temperature in a molten slag environment with the evolution of magnesium vapor at about atmospheric (reaction-equilibrium) pressure—making feasible a continuous or semi-continuous process. A fifth and very important advantage is the recoverability of alumina from the resulting slag, which in turn reduces the net ratio of slag to magnesium substantially, to between about 3 to 1 and 2 to 1, or even lower.

In another art, in commercial use on a small scale, is the "Pedersen Process," for the production of alumina for aluminum cell feed from low grade bauxite (ferruginous or siliceous or both) by smelting bauxite together with lime and carbonaceous reducing agent in a submerged-arc type electric furnace to produce a low grade iron product and a calcium-aluminate slag from which Al_2O_3 can be recovered. Unhappily, the Al_2O_3 recovered contains SiO_2—sufficiently troublesome in an aluminum cell feed, in some cases, to require a separate "desilication" treatment. See H. E. Blake, Jr., Bur. Mines Rept. Inv. 6939 (1967). In contrast, the slag herein produced may be silica-free, and pure alumina may be recovered without desilication.

BRIEF DESCRIPTION OF THE INVENTION

The present invention may be characterized as an aluminothermic process for the production of magnesium metal and a calcium-aluminate slag containing recoverable alumina by the reduction of magnesium oxide with substantially pure aluminum in a reaction zone at an elevated temperature wherein: the oxide charge contains MgO and CaO in a weight ratio of between about 1.1 and 2.3; the reducing agent comprises at least 85 percent aluminum; and the slag produced as a by-product of the reaction has a composition of about 35–65 percent alumina, 35–55 percent calcium oxide and 0–10 percent silica and, when removed from the system, contains less than 5 percent magnesia.

This process is capable of substantially continuous operation at about atmospheric pressure. The process also allows substantially full utilization of the magnesia and reductant charged. The weight ratio of slag to magnesium may be held to a range of about 2–3:1. Pure aluminum oxide may be extracted from the slag, since when cooled and solidified it is composed primarily of the soluble calcium aluminates, $12CaO \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$. When aluminum oxide is recovered from the slag, the residual $CaCO_3$ (to magnesium) ratio will generally range from about 2.8:1 to 1.4:1. Moreover, the residual $CaCO_3$ can be converted to CaO and recycled—thereby decreasing the net slag (i.e. solid residue) ratio almost to zero.

BRIEF DESCRIPTION OF THE DRAWINGS

The attached figures are presented to illustrate a complex process embodying the present invention in preferred form.

FIG. 1 is a block diagram of that part of the present process wherein magnesia and calcined dolomite are reacted in a magnesium furnace with substantially pure aluminum to obtain magnesium by vaporization and condensation and a calcium-aluminate slag by-product.

FIG. 2 is a block diagram of part of the present process, wherein the calcium-aluminate slag by-product is leached in order to obtain purified alumina.

DETAILED DESCRIPTION OF THE INVENTION

General definitions

Several terms are used herein which need definition. The reducing agent in the magnesium furnace is "substantially pure aluminum." This includes not only pure aluminum but aluminum alloys containing at least 85 percent aluminum by weight (including the following alloys by standard number: 13, 380, 43, 195, 214 and 220), and aluminum scrap materials, generally having an aluminum content of at least 95 percent (by numbers: 1100, 3003, 2017, 2024, 5052, 6063 and 7075). In general, silicon may constitute up to 10 percent or even slightly more of the reducing agent (e.g. 12 percent in alloy 13), if a disintegrating slag is desired. It is preferred that the remaining components, such as manganese, calcium, chromium or magnesium*, constitute less than 5 percent of the reducing agent by weight.

The term "calcium-aluminate slag" refers to that part of the reaction media constituting the oxide by-products of the reaction. These oxides are principally calcium oxide and alumina, but may include silica or other oxides. As herein defined only the calcium oxide, alumina and silica are significant, and the composition will contain as various complex oxides: 35–55 percent CaO, 35–65 percent Al_2O_3 and 0–10 percent SiO_2. Up to 5 percent or even more of other oxides may be disregarded. However, the slag as tapped must not contain more than 5 percent MgO, and, if alumina is to be recovered in reasonable yield, no more than 2 percent MgO and preferably as little as possible. The term "molten" applied to such slag means that at least a major part of the slag is in a liquid state. This generally occurs in the range of composition for the present invention at 1300–1700° C.

Other terms used herein, such as "inert gas" and "substantially static," are defined in my co-pending applications Ser. Nos. 796,214 and 26,118.

The calcium aluminate slag by-product

A vital element in the present process is the calcium-aluminate slag, which together with the melted reducing agent constitutes the liquid medium in the magnesium furnace. The composition of the slag is important from two aspects. First, it is essentially the reaction medium wherein magnesium oxide is reduced to magnesium and concurrently in turn the reducing agent aluminum is oxidized to alumina. (Any silicon present in the reducing agent may or may not be oxidized.) Second, if the composition of the slag is properly controlled, it can be a valuable by-product, providing alumina for use as cell-feed or other purposes such as high quality refractories.

In the Al_2O_3-CaO-SiO_2 tertiary system, $CaO.Al_2O_3$ and $12CaO.7Al_2O_3$ are almost completely soluble in a leaching solution of sodium carbonate; but $3Ca.Al_2O_3$ is less than 50 percent soluble, $CaO.2Al_2O_3$ is almost completely insoluble and $2CaO.Al_2O_3.SiO_2$ is insoluble. To maximize aluminum oxide recovery, it is desirable to produce a spent oxide with as much as possible of its aluminum oxide content in the form of crystalline calcium aluminates. See generally, Bur. Mines Rept. Inv. 6939, supra, 4–13 and "Recovery of Alumina and Iron from Pacific Northwest Bauxites by the Pedersen Process," O. C. Fursman et al., Bur. Mines Rept. Inv. 7079, 1968, 4–15.

Controlled cooling of the molten slag maximizes alumina recovery. The proper cooling rate is a function of slag composition; generally, a slag with a substantial silica content must be cooled more slowly than one with a lower amount or none. Further, it is desirable that the cooling rate be slow enough so that the two phase transformations of dicalcium silicate ($2CaO.SiO_2$), alpha to beta at 1420° C. and beta to gamma at 675° C., be allowed to occur, since the inversion to the gamma form is accomplished by a 10 percent increase in volume, which can shatter the cooled residue into a fine dust, a phenomenon commonly called "dusting." Too rapid cooling prevents crystallization and produces a glassy solid from which aluminum oxide extraction is poor.

*Magnesium may be present in the reducing agent but, as should be obvious, it should not count in determining its composition for the purposes of this invention. It will be distilled into the product.

The silicon dioxide content of the slag must be at least about 5 percent to effect dusting. Dusting greatly reduces the amount of crushing required before the aluminum oxide can be extracted. However, as shown in the examples, a very high recovery of aluminum oxide, up to 97.5 percent, is possible when the silicon dioxide content is less than 4 percent, too low for appreciable dusting. Thus, the desirability of having enough silicon dioxide for dusting must be balanced against the desirability of the high total recovery of aluminum oxide. (If the slag contains enough SiO_2 to cause dusting, the Al_2O_3 product is likely to contain more SiO_2 than is permissible in cell feed, and a separate desilication step may be required.) The silica may be not only derived from silicon, but may be alternatively that silica from the original oxide charge (e.g., magnesite). On balance, silica is neither necessary nor preferred.

The aluminium oxide content of the slag should be high, to minimize the amount of slag to be processed per unit of Al_2O_3 recovered. The calcium oxide content should be low, and need not exceed that needed to form soluble calcium aluminates.

The presence of magnesium oxide in the slag, however, severely affects recovery of aluminum oxide, because it has been found that a mole of MgO can tie up four moles of Al_2O_3 in the insoluble complex

$$6CaO.4Al_2O_3.MgO.SiO_2$$

Thus, the slag is tapped periodically when its MgO content has been lowered to less than 5 percent. Preferably substantially all of the magnesium oxide is depleted from the reaction zone (leaving less than 2 percent) before the slag is removed.

Weighing all these factors, the range for the tertiary composition of the spent oxides, exclusive of minor amounts of other oxides (if present), is as follows: 35–65 percent aluminum oxide, 35–55 percent calcium oxide and 0–10 percent silicon dioxide.

Alumina recovery from slag by-product

Exhaustive studies of the Pedersen process have been carried out by the U.S.B.M. with the objective of determining whether it can be used successfully for the recovery of Al_2O_3 at reasonable cost from low quality alumina-bearing ores such as low grade bauxite and clay. We are not concerned here with the smelting operation for the production of slag, which has no counterpart in the present process, but only with the leaching operation.

Results of immediate interest here may be summarized:

For high leachability it is not necessary to produce a distintegrating slag. The oxidic compounds $CaO.Al_2O_3$ and $12CaO.7Al_2O_3$, when produced synthetically in crystal form and properly ground, are completely soluble, or nearly so, in straight Na_2CO_3 solutions (no free NaOH) at temperatures of about 70° C. and a leaching time of one or two hours. All other calcium aluminate compounds are either insoluble or difficultly soluble in such a solution.

Within the range of slag compositions given above, the two calcium aluminates shown are the only ones which are formed. In order to obtain them in crystalline form, the slag must be cooled very slowly, but this can easily be done.

If there is a substantial amount of SiO_2 in the slag, usefulness of the Al_2O_3 as aluminum cell feed is restricted. In some cases this problem must be overcome by a separate "desilication" step, which increases the cost of Al_2O_3. Avoidance of this problem is a major reason for the production of an essentially SiO_2-free slag as the preferred form of the process of the invention.

If MgO is present in the slag, even in small proportions, it has a very deleterious effect upon the recovery of Al_2O_3. As the slag cools, there is formed a complex oxidic compound, $6CaO \cdot 4Al_2O_3 \cdot MgO \cdot SiO_2$, which is practically insoluble in the leaching operation. Thus one mole of MgO in the slag not only ties up four moles of Al_2O_3 with loss of recovery; it also ties up six moles of CaO. However, the activity of Al in the system is so high that a finished slag containing little or no MgO can be produced. This may require a brief finishing-off period before the slag is tapped.

The substantially pure aluminum reducing agent

Substantially pure aluminum permits vigorous reduction of magnesium oxide to magnesium and the evolution of magnesium vapor from the molten slag at about one atmosphere total pressure. As mentioned above, the aluminum may be composed of pure metal, high-aluminum alloys or aluminum scrap metal, including alloys. The compositions of the principal aluminum alloys and aluminum scrap materials produced by their fabrication are given below in Table 1.

The aluminum reducing agent may be derived, in part, by reduction of alumina recovered from the slag byproduct to obtain aluminum to be recycled to the reducing agent feed.

It might be supposed that the presence of metallic impurities in aluminum scrap used as reductant in the present process would present serious or even insuperable problems in its use for such a purpose. In fact, this is not the case, and most of these "impurities" provide positive credits either to the cost of production or to the total value of the magnesium produced.

TABLE I.—COMPOSITION OF ALUMINUM ALLOYS

Number	Al	Mn	Cu	Cr	Zn	Si	Mg
1100	99+						
3003	Bal.	1.2					
2017	Bal.	0.5	4.0				0.5
2024	Bal.	0.6	4.5				1.5
5052	Bal.			0.25			2.5
6063	Bal.					0.4	0.7
7075	Bal.		1.6	0.3	5.6		2.5
13	Bal.					12	
380	Bal.		3.5			9	
43	Bal.					5	
195	Bal.		4.5			0.8	
214	Bal.						3.8
220	Bal.						10

The low-price scrap materials may be used readily in the present process, and this factor is very important to its economics. The principal impurities in the aluminum alloys and scraps are magnesium, silicon, copper, manganese, chromium and zinc, usually less than 5 percent by weight. Alloy 13 has 12 percent silicon and alloy 220 has 10 percent magnesium, but plainly these impurities present no problem and can be utilized fully in the present process.

Copper is present in proportions up to 4.5 percent in several alloys; it is inert in the process and will form part of the molten metal "heel" in the bottom of the furnace. The same holds for chromium which is present in small amounts in a few alloys.

Manganese is present in amounts ranging from 0.6 to 1.2 percent in a few alloys, and since its vapor pressure is about 10 mm. Hg at 1500° C., some manganese vapor will be carried over with the magnesium vapor into the product. Since actual operations use a mixture of all kinds of scrap, most of which do not contain manganese, it is improbable that this impurity will create serious problems. But if it does, then either manganese-bearing scrap must be eliminated, or used separately to produce magnesium for use as alloys of aluminum containing both manganese and magnesium—of which there are several.

The impurity which could cause trouble is zinc, which has a boiling point of 907° C., so that any zinc present in the scrap will be carried over into the magnesium produced. However, there appears to be only one alloy containing zinc (about 5.6 percent).

The oxide charge containing magnesia

The oxide charge contains magnesia and preferably calcined dolomite. The magnesia is of course reduced by

the substantially pure aluminum reducing agent. The ratio of MgO to CaO in the charge is about 1.1 to 2.3 by weight. Dolime provides both constituents in a 1:1 mole ratio; magnesia may be used to supply MgO, and lime, to supply CaO.

The calcium oxide is carried through to the slag by-product where, upon solidification, it combines with Al_2O_3 to form the desired calcium aluminates. Part, or even all, of the required calcium oxides may be added as lime, but this is not generally preferred, since usually dolomitic lime is available to provide not only the required calcium oxide but also magnesium oxide.

Low cost magnesia can be obtained in several ways, at suitable locations: (a) production of MgO from sea water, brines, or bitterns by methods which are well known; (b) the use of low-grade magnesite not suitable for refractory purposes and therefore available at low cost. Such ores are generally available as waste from refractory grade magnesia operations, or as low grade ore deposits not presently worked. Such low grade ores usually contain both CaO and SiO_2 in relatively small proportion to MgO.

The presence of CaO in small proportion in such ores is of course not detrimental, because CaO is required in the process, but the presence of SiO_2 requires careful consideration. If SiO_2 is present in a calcium-aluminate slag of the type contemplated, when the slag solidifies it will form the relatively insoluble compound $2CaO \cdot SiO_2$. In proportions from about 5 percent to 10 percent SiO_2 by weight the result is a slag which disintegrates or "powders" when cooled very slowly to permit phase changes of the crystalline silicate to take place.

Furnace construction

An important problem incidental to the present process is the provision of a refractory furnace lining which will hold the molten slag at 1500° C. or more, by forming a self-perpetuating solid lining between the graphite lining which protects the furnace shell, and the molten slag, which would otherwise attack the graphite with disastrous results.

In the Magnetherm process, magnesia is used for this purpose, and it serves very well because it is not appreciably attacked by the high-lime calcium aluminum silicate slag used in that process, whereas the molten calcium aluminate slag used in the present process may be expected to attack MgO quite readily. However, a study of the slag phase diagram for calcium aluminate slags shows that if alumina is used as the refractory, any attack upon it by the molten slag will cause an increase in the Al_2O_3 content of the film of slag at the surface of the lining, with the result that eventually an inner shell of slag containing more than about 65 percent Al_2O_3 will form and soldify. This happens because of the fortunate circumstance that the lowest melting point of calcium aluminate slags is 1400° C. at about 54 percent Al_2O_3, which is near the median of the proposed range of slag composition, and as the Al_2O_3 content of the slag increases the melting point increases steadily and sharply to 1550° C. at 60 percent Al_2O_3 and 1650° C. at 70 percent Al_2O_3.

Modifications dependent upon economic considerations

The economics of this process are such that if in special circumstances scrap aluminum and other raw materials are cheap enough, and Al_2O_3 is below its normal value, the slag can be discarded or sold at a low price. In such case, it might be desirable to use an alloy with silicon content up to 10 percent to produce a disintegrating slag.

It is also possible that situations exist where low quality magnesite or the like is available at such low cost as to affect the entire economics of the process. Such magnesites are available at numerous places, especially as waste or discard from the production of refractory grade MgO. Deposits of magnesite or magnesitic dolomites, unsuitable as a source of refractory grade magnesia, are also available for use herein.

Such magnesites usually contain both SiO_2 and CaO as the undesirable impurities. For use in the present process the CaO is not only acceptable but has some small value. The SiO_2 content, within reasonable limits, can be used to produce a distintegrating slag from which Al_2O_3 can be recovered. As with the case mentioned above, it is a matter of economics whether the low cost of MgO, plus the cost of pulverizing a nondisintegrating slag, counterbalances the somewhat lower recovery of Al_2O_3 and somewhat higher leaching costs, plus the disadvantage of an undesirably high SiO_2 content of the Al_2O_3 produced.

Other conditions

The residual aluminum, in the slag during the "finishing-off" period, will be distilled over into the magnesium.

During the "finishing-off" operation, neutral gas is introduced into the system to replace magnesium vapor and maintain atmospheric pressure, but in a properly designed system this will be automatic and in any case does not represent a serious operating problem. When slag or magnesium are tapped from the furnace or crucible, the pressure of neutral gas can be raised above atmospheric to force them out of the system without use of a pump. If the use of scrap aluminum results in accumulations of non-volatile metal such as copper, it can be permitted to accumulate up to the level of the slag tap hole, after which it will be vented along with the slag and form a regulus at the bottom of the slag pot.

The use of inert gas

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 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 desired to recover inert gas.

In a further embodiment of the present invention, the product magnesium is vaporized and evolves from the reaction medium through a substantially static atmosphere of inert gas and passes predominately by diffusion through the inert gas from the reaction zone to a condensation zone and is collected. This modification allows operation at a higher absolute pressure and also yields a magnesium product relatively pure as compared with commercial magnesium, containing impurities, notably silicon, in low concentration; see my co-pending application Ser. No. 26,118, filed on Apr. 6, 1970.

Other embodiments using inert gas are also possible, for example, to increase the partial pressure of the system, as disclosed in my co-pending application Ser. No. 796,214, U.S. Pat. No. 3,658,509, or as another method of maintaining a positive pressure in the system during slag tapping. In this use, the excess gas would be added to the system just before the slag is to be tapped, and removed, for instance by bleeding or by a vacuum pump, before charging of the reactants is recommenced.

Examples

The following operations are conducted in an electric reducing furnace coupled with a condensing chamber. The procedure is to charge the furnace with components to produce a slag of the desired composition, and to supply heat until a proper viscosity is reached at a temperature above about 1300° C., whereupon the oxide charge and the reducing agent are charged continuously in intermittent, small batches. When a large quantity of slag accumulates, the reaction is allowed to run until all or substantially all of the magnesium oxide content of the slag is reduced to magnesium. The major portion of the molten slag, and of spent alloy, if any, is then tapped, leaving enough slag and alloy to repeat the cycle. The addition of the oxide charge and the reductant, and the tapping of the slag

and alloy are conducted in such a manner that, disregarding the fluctuations in the level of magnesium oxide, the composition of the slag is maintained substantially constant. The operation is conducted substantially continuously.

Attached Table II summarized stoichiometric data of examples having raw materials and slag compositions chosen to illustrate limiting and normal slag compositions; the use of pure aluminum (>99%) and of three alloys with extreme compositions with respect to alloying ingredients; and the use of a low-grade magnesia produced by calcining magnesite containing about 8 percent of SiO_2. It has been assumed that all of the CaO required for the

TABLE II.—STOICHIOMETRIC DATA FOR REACTIONS USING TYPICAL ALLOYS, DOLIME AND MAGNESIA

	Example						
	A	B	C	D	E	F	G
Alloy number	1100	1100	1100	1100	13	220	7075-0
Al, percent	100	100	100	100	88	90	9
Mg, percent						10	2.5
Si, percent					12		
Zn, percent							5.6
Cu, percent							1.6
Other							0.3Cr
Slag:							
Al_2O_3	50	57.5	65	55	55	57.5	60
CaO	50	42.5	35	37.9	36.5	42.5	40
SiO_2				7.1	8.5		
M.p., ° C	1,400	~1,530	~1,600	~1,550	~1,550	~1,500	~1,550
	Units per magnesium produced						
Raw materials:							
Dolime	2.45	1.80	1.33	1.69	1.38	1.65	1.48
Magnesia	0.64	0.92	1.11	0.97	1.10	0.85	0.96
Alloy	0.75	0.75	0.75	0.75	0.73	0.77	0.82
Products:							
Slag	2.84	2.47	2.19	2.58	2.21	2.27	2.315
Magnesium	1.00	1.00	1.00	1.00	1.00	1.00	[1] 1.045

[1] Case G—1.00 units magnesium and 0.045 units zinc.

NOTE.—The magnesium produced will contain up to 20 percent Al. This has been ignored in the above data because the reactions are not affected by distillation of aluminum from reaction zone to condenser. Case A slag is almost exactly $12CaO \cdot 7Al_2O_3$ (50.5% Al_2O_3). Case C slag is almost exactly $CaO \cdot Al_2O_3$ (64.6% Al_2O_3). Case B slag is the median composition between A and C. Case D slag derives SiO_2 from 1.14 units magnesia containing 16% SiO_2. Case E assumes 100% utilization of Si content of alloy. Cases D and E slag will disintegrate.

slag will be derived from calcined dolomite, i.e. dolime, and that any additional MgO required will be supplied as comparatively pure MgO derived from sea water, bitterns, or other sources. These examples are given to illustrate the flexibility of the process with respect to raw materials on the one hand, and on the other hand to show the narrow range of slag compositions from which nearly complete extraction of Al_2O_3 can be obtained.

Example A shows a slag which will solidify as crystalline 12 $CaO.7Al_2O_3$ which is completely soluble in soda ash solutions. It represents the lower desirable limit of Al_2O_3 for a silica-free slag, because if CaO is greater than about 50 percent the relatively insoluble compound $2CaO.AlO_3$ will be formed, thereby decreasing Al_2O_3 recovery.

Example C shows a slag which will solidify as crystalline $CaO.Al_2O_3$ which is also completely soluble in soda ash solution. It represents the upper desirable limit of Al_2O_3 for a silica-free slag, because if CaO is less than about 35 percent, the relatively insoluble compound $CaO.2Al_2O_3$ will be formed, thereby decreasing Al_2O_3 recovery.

Example B shows a median slag between A and C, where the solid slag will be a mixture of crystalline $12CaO.7Al_2O_3$ and $CaO.Al_2O_3$, both of which are completely soluble. The preferred slag of the invention is this type of mixed composition, but it is of course possible to operate somewhat outside the indicated preferred limits without departing from the spirit of the invention.

Examples D and E show slags containing enough SiO_2 to cause disintegration, thus avoiding the necessity of grinding a non-disintegrating slag. But in such slags the Al_2O_3 content is not completely recoverable, and there is an additional sludge problem. However, in Example D the SiO_2 is supplied by using a low-grade siliceous magnesia which at certain locations could provide a substantial cost advantage. The magnesite used to produce the calcined magnesia could contain nearly 9 percent SiO_2. In Example E the SiO_2 is supplied by using as a supplementary reductant the silicon contained in a silicon-aluminum alloy, which can also result in a substantial cost advantage.

For a further example, as a modification of Example D, a calcined magnesia containing about 27 percent SiO_2 could be used to produce slag having the composition: Al_2O_3, 49 percent; CaO, 41 percent; SiO_2, 10 percent. This requires additional dolime to provide CaO to bind the extra SiO_2, and about 1.46 units of siliceous magnesia after adjusting for the MgO content of the additional dolime. The slag ratio will thus be roughly 2.9 per unit of magnesium, but a low-grade magnesite containing as much as 15 percent SiO_2 could be used to provide the siliceous magnesia.

If Al_2O_3 is extracted from the lag, and the residual $CaCO_3$ is calcined and recycled, there is substantially no residue. The process is then a closed cycle, with MgO and Al in, Mg and Al_2O_3 out.

Moreover, as mentioned previously, the Al_2O_3 by-product can be reduced to provide an aluminum recycle to reducing agent feed.

Data for Examples 1–7 are shown in Table III. In the reducing agent, the materials other than aluminum and silicon metal are omitted; and in the oxide charge, it is assumed that the magnesia and dolomitic lime are pure MgO and $MgO \cdot CaO$, respectively, in that the impure oxides are omitted. The composition of the slag resulting from complete reaction of the reducing agent with the MgO in the oxide charge is given. In order to obtain the proper calcium-aluminate slag for Example 3 an additional quantity of lime was added.

It can be seen that a very high recovery of alumina is obtained. It can also be seen how the removal of recoverable alumina from the slag reduces the total slag ratio, as represented by the waste slag produced, to a very low level, in some cases approaching or even exceeding one part waste slag by weight per part of magnesium produced.

In Example 4, the insoluble $2CaO \cdot SiO_2$ constitutes about 18 percent of the slag by weight. Since this increases the resulting waste slag ratio, it is apparent why the substantially pure aluminum is preferred over re-

ducing agents containing relatively high amounts of silicon metal for the present process.

The figures

The attached figures illustrate schematically an aluminothermic process, broken into two parts, embodying the present process. It can be seen that the products of the main part are magnesium, calcium aluminate and a small amount of residual metal (FIG. 1). The calcium aluminate may be treated (FIG. 2) to produce cell-grade alumina and $CaCO_3$ or CaO—the latter of which may be recycled to supply part of the lime of the first part (FIG. 1). Thus, the net effect, somewhat simplified, can be to produce magnesium and cell-grade alumina from aluminum and magnesia—the products may be pure, but the reactants need not be.

TABLE III

Example	1	2	3	4	5	6	7
Reducing agent:							
Al	93.2	84.4	85.0	90	86.2	94.6	89.3
Si	6.8	15.6	15.0	10	13.8	5.4	11.7
Oxide charge:							
Magnesia [1]	.502	.597	1.68	0.90	.858	.832	1.08
Dolomite lime [1]	2.79	2.58	0	1.88	1.95	1.50	1.42
CaO added [1]	0	0	1.31	0	0	0	0
SiO_2 added [1]	0	0	0	0	0	0	0
Slag: [2]							
Al_2O_3	43.1	40.0	42.9	50.0	46.5	57.6	55.2
CaO	53.7	52.6	48.5	43.8	45.0	38.7	36.9
SiO_2	[6] 3.2	8.4	8.6	6.2	8.5	[6] 3.7	7.4
Slag produced	3.06	2.87	2.69	2.52	2.52	2.30	2.24
Percent Al_2O_3 recoverable [3]	62.7	[5] 7.45	89.8	>90	91.0	97.5	44.2
Waste slag produced [1] [4]	2.22	2.04	1.67	>1.39	1.45	0.99	1.68

[1] Expressed as unit weight per unit of magnesium produced.
[2] The slag percent is calculated as follows: $SiO_2+Al_2O_3+CaO$—(CaO equivalent for any TiO_2 present)=100%.
[3] 15.0 grams of slag leached with 11.0 grams Na_2CO_3 in 250 milliliters of H_2O at 25° C.±5° C. for 16 hours.
[4] Waste slag produced is calculated as follows: Slag produced—(Weight Al_2O_3)×(percent Al_2O_3 recoverable).
[5] Examples 2 and 3 show the difficulty presented when a slag is not properly crystallized to improve the recovery of aluminum oxide. Slag No. 2 was not cooled slowly enough to permit adequate crystallization, whereas No. 3 was cooled slowly under proper control.
[6] The silicon dioxide content of these slags is too low to produce appreciable dusting, even when the slag is cooled slowly.

I claim:

1. An aluminothermic process for the production of magnesium, which comprises charging to a reactor an oxide mixture containing magnesium oxide and calcium oxide, and a metallic reducing agent comprising at least 85 percent aluminum; maintaining in said reactor a molten calcium-aluminate slag bath; removing, when the magnesium oxide content of said slag is less than 5 percent, calcium aluminate comprising 35–65 percent Al_2O_3, 35–55 percent CaO and 0–10 percent SiO_2; evolving magnesium vapor from said reactor to a condenser; and condensing and recovering said magnesium.

2. The process of claim 1, wherein said oxide mixture comprises MgO and CaO in a ratio by weight of between 1.1:1 and 2.3:1.

3. The process of claim 1, wherein said removed calcium aluminate comprises 51–65 percent Al_2O_3 and 35–49 percent CaO.

4. The process of claim 1, wherein said reactor and condenser contain inert gas at a partial pressure of at least 0.1 atm.

5. The process of claim 1, wherein evolution of said magnesium vapor is induced by a stream of inert gas passing from said reactor to said condenser.

6. The process of claim 1, wherein said magnesium vapor evolves from said reactor to said condenser predominately by diffusion through a substantially static atmosphere of inert gas.

7. The process of claim 1, wherein said oxide mixture comprises magnesia and calcined dolomite.

8. The process of claim 1, wherein said magnesium oxide is derived at least in part from a siliceous magnesite.

9. The process of claim 1, wherein said oxide mixture comprises free lime.

10. A process for the production of magnesium and alumina, which comprises:

(a) charging to a reactor an oxide mixture containing magnesium oxide and calcium oxide, and a metallic reducing agent comprising at least 85 percent aluminum; maintaining in said reactor a molten calcium-aluminate slag bath; removing, when the magnesium oxide content of said slag is less than 5 percent, calcium aluminate comprising 35–65 percent Al_2O_3, 35–55 percent CaO and 0–10 percent SiO_2; evolving magnesium vapor from said reactor to a condenser; and condensing and recovering said magnesium; and

(b) solidifying and grinding or dusting said calcium aluminate into particulate form; leaching said particulate calcium aluminate to obtain $Al(OH)_3$; and calcining said $Al(OH)_3$ to obtain purified alumina.

11. The process of claim 10, wherein said removed calcium aluminate comprises 51–65 percent Al_2O_3 and 35–49 percent CaO.

12. The process of claim 10, wherein said reactor and condenser contain inert gas at a partial pressure of at least 0.1 atm.

13. The process of claim 10, wherein calcium oxide is recovered from said particulate calcium aluminate and recycled to constitute a portion of said oxide mixture.

14. The process of claim 10, wherein said purified alumina is reduced to aluminum metal, and said aluminum metal is recycled to constitute a portion of said metallic reducing agent.

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