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THERMAL REDUCTION OF OXIDIC MAGNESIUM ORE

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1

This invention relates to methods of recovering metallic magnesium from its ores by heating a mixture of ore and reducing agent, with and without other substances, at temperatures at which the magnesium metal reduced from the ore is distilled from the reaction mass, and thereafter condensing the magnesium vapors to recover that metal in solid form.

Such processes as just generally described are conventional and have taken many specific forms, none of which have been particularly successful commercially. While the thermal processes of directly reducing or distilling magnesium and recovering the vapor are inherently simpler than those processes which are based upon the electrolysis of magnesium chloride and by which most magnesium metal is now produced, the simplicity is more apparent than real. The fundamental difficulty with the thermal production methods of making magnesium is one of cost. The comparatively high cost of such processes arises primarily from the following factors:

First, the reduction agents heretofore proposed, which are otherwise generally operable, are relatively high in cost, except for carbon which has the inherent disability of producing a gaseous reaction product, carbon monoxide, which reacts with the magnesium vapor to again form magnesium oxide. No inexpensive and positive method of treating the mixture of magnesium vapor and carbon monoxide produced by the carbon reduction has yet been developed with the result that the product of this reduction must be again treated in an expensive and separate step to reduce its magnesium oxide content.

Second, thermal processes necessarily operate at high temperatures and require expensive apparatus, including furnaces, retorts, vacuum pumps and similar equipment and a high incidence of labor. Moreover, this equipment must be made of materials which withstand high temperatures. Such materials are expensive and deteriorate rapidly at the temperatures used.

Third, the use of any reduction agents, even those such as aluminum, silicon, ferrosilicon, calcium carbide, silicon carbide, silicides and others, which do not produce a gaseous product of reaction which will seriously react with the magnesium vapor, has to date been limited to batch operations because of the difficulties of conducting the operation continuously, said difficulties being inherent in the high temperatures involved and the desirability of using vacuum distillation to avoid the use of even higher temperatures.

Fourth, although it is possible to conduct ther-

2

mal reduction operations utilizing these reduction agents in a continuous manner, the equipment necessarily involved in the upkeep of that equipment is very expensive and impractical.

For these and other reasons magnesium cannot, at present, be thermally reduced at prices which will commercially compete with magnesium produced by the electrolysis of magnesium salts, such as magnesium chloride.

The object of the present invention is to provide an improved process, the improvement consisting in the use of a novel reducing agent, by which the thermal reduction of magnesium from its ores may be carried out at costs lower than those heretofore encountered in thermal reduction processes. A further object is the provision of a new and novel method of reducing magnesium from its ores.

This invention provides a thermal reduction process so reduced in cost as to compete commercially under favorable conditions with present electro-chemical methods.

In the practice of the invention I employ as a reducing agent aluminum carbide and in the preferred and, under present conditions of the art, competitive form I employ a modification thereof containing as active components aluminum carbide and aluminum. While this aluminum carbide-aluminum mixture could be made from pure substances, such as pure carbon and pure alumina, considerations of cost and efficiency are in favor of the use of a reducing agent which is itself the product of the reduction of aluminous ore with carbon. Thus the preferred reducing agent is made by mixing an aluminous ore, such as bauxite, with a commercial carbon, such as ordinary coke, and reacting the mass at high temperature under circumstances somewhat different, and less expensive, than would be employed if it were the purpose of the process to reduce the aluminum oxide or the aluminous ore entirely to pure aluminum, and to prevent the formation of aluminum carbides which are usually an unwanted material in commercial aluminum.

Despite the fact that much of the aluminum in this partially reduced mixture is in the form of aluminum carbide, the mixture is highly efficient as a reducing agent when reacting with a magnesium oxide ore, such as calcined dolomitic limestone or calcined magnesite. When this mixture is used as the reducing agent, its ratio of efficiency to cost is high, as compared to known reducing elements, as will herein be discussed and demonstrated.

The aluminum carbide-aluminum mixture may be made in various specific ways and in various purities. One form that I have found suitable is that obtained by mixing low grade bauxite and coke and subjecting the mass to the heating of an arc with the result that there is produced a solid lump of reaction product surrounded by unreacted charge. After the furnace is cool enough to handle this lump, it may be readily separated from the loose granular unreacted charge and may be prepared for use by a simple pulverizing process, since this reaction product tends to be friable and pulverant, an item which in itself considerably reduces the cost over the use of aluminum, which must undergo an expensive granulating or pulverizing step before it can be satisfactorily used as a reducing agent in connection with magnesium ores. Such reaction products may vary in composition but are composed principally of aluminum carbide and metallic aluminum, of doubtful purity. A typical product contained the following:

	Per cent		Per cent
Al ₄ C ₃	38.73	Ti	2.62
Al	40.95	Fe	3.44
AlN	0.12	Si	2.27
Al ₂ O ₃	1.63	C	0.92
CaO	2.52		

all percentages being by weight. The impurities, such as iron, titanium, silicon and calcium, are the result of the original content of the impure aluminum ore and may even be helpful, and at least not harmful, when this product is used as a reducing agent for the reduction of magnesium. The actual cost of production of this product is an interesting feature in the economies which are obtained by the use of this material as a reducing agent. Both the aluminum carbide and the aluminum of the mixture are produced at low cost, the latter at about one-half the kilowatt hours per pound necessary to the production of commercial aluminum, and this single factor is quite apart from the other expensive steps in the production of commercial aluminum, such as beneficiation of ore to obtain a pure alumina, the use of carbon in the form of pure electrodes instead of in the commercial and cheap form of coke, etc., all of which are avoided. The cost of this material is equally interesting when compared with ferrosilicon, in which silicon is the reducing agent, the power consumed in the preparing of ferrosilicon being in the neighborhood of about one-fourth more per pound than the cost of preparing the aluminum carbide-aluminum reduction product.

In practicing the process of this invention the

finely ground reactants are thoroughly mixed and, preferably, compressed into pellets or briquettes. Better results are obtained if all of the reactants are of a size passing a standard 100 mesh screen, although such refinement is not necessary. The efficiency of the reaction is increased by the addition to the mixture of fluorides or chlorides, as is likewise true in prior processes for the thermal reduction of magnesium ore, but in my improved process certain fluorides and chlorides and certain mixtures thereof are particularly efficacious as will, hereinafter, be described. Magnesium oxide or any ore containing magnesium oxide, such as dolomite or magnesite, may be used as the source of magnesium. Where the magnesium is in the ore in the form of carbonate, it is preliminarily calcined to drive off carbon dioxide and thus reduce the carbonate to oxide. I include magnesium oxide, ores containing that oxide and calcined carbonate ores in the term "oxidic magnesium ore." The temperature at which the reaction best takes place is, of course, the lowest temperature consistent with good results, and it is a feature of my invention that where the mixture is heated in vacuo the process thereof may be operated efficiently at temperatures as low as 1100° C., which temperature is lower than the efficient operating temperatures employed with other comparable processes using known reducing agents. Good results can, however, be obtained at temperatures as low as 900° C. When the reaction mixture is heated at atmospheric pressures higher temperatures are necessarily employed for equivalent results, but temperatures above about 1500° C. are not generally desirable or efficient.

The reduction agent and the oxidic magnesium ore may be mixed in various proportions. It is wasteful and inefficient to use ore in such amount that its magnesium oxide content is less than that required to react with the aluminum carbide and aluminum in the reduction agent. At least stoichiometric proportions of magnesium oxide and aluminum carbide and aluminum should be used, and I have found that when the magnesium oxide is in excess the efficiency of the reaction is greatly increased.

Following in tabular form are the results obtained with various indicated reaction mixtures in the practice of the invention, all of the results being obtained by heating the dry briquetted mixture at indicated temperatures and in indicated vacuum for stated periods of time and condensing the metallic vapor distilled from the reaction mass. In each case the reducing agent used was a product obtained by the reduction of bauxite by coke, all as above set forth.

Run No.	Components of reaction mixture other than the reduction agent		Relation of MgO in mixture to available aluminum	Approx. temp., °C.	Time, hrs.	Vacuum mm. of mercury	Yield per cent of Mg available in reaction mixture
	Ore	Other per cent by weight					
1	Calcined magnesite		Stoichiometric	1,200	3	0.15	60.5
2	do		do	1,100	3	0.15	38.1
3	do		do	1,200	3	0.20	79.5
4	do	10% MgF ₂	About 30% excess MgO	1,100	3	0.20	69.6
5	do	8.5% CaF ₂	do	1,000	3	0.10	43.1
6	do	8.5% MgF ₂ , MgCl ₂	do	1,100	3	0.10	87.4
7	do	do	do	1,000	3	0.15	57.5
8	do	2.5% MgF ₂ , 2.5% CaF ₂	Stoichiometric	1,100	3	0.20	75.5
9	do	5% CaCl ₂	do	1,100	3	0.20	85.9
10	Calcined dolomite (40% MgO) content	5% CaF ₂	do	1,100	3	0.20	84.7
11	do		do	1,100	3	0.35	82.2
12	do	5% CaF ₂	do	1,100	6	0.20	96.0
13	do	do	About 25% excess MgO	1,100	3	0.20	92.1

5

Referring to the results shown in said tabulation, it will be noted that an excess of MgO in the reaction mixture is beneficial; that rising temperature produces more efficient results (compare runs 1 and 2); that increase of time increases yield (compare runs 11 and 12) and that the use of fluorides and chlorides increases the efficiency of the reactions (compare runs 1 and 3; runs 10 and 11; runs 1 and 9; runs 1 and 8).

Moreover it will be noted that with the use of fluoride or chloride and with or without an excess MgO present, the results obtainable at temperatures of 1200 can be approximately duplicated by 1000° C. and exceeded at 1100° C. (compare runs 1 and 7; runs 1 and 8; runs 1 and 9; runs 2 and 5; runs 1 and 6).

It will likewise be noted that calcium chloride is more efficient than magnesium fluoride or calcium fluoride or mixtures thereof but that a double salt of $MgF_2 \cdot MgCl_2$ is equally efficient.

6

and depreciation of the relatively expensive equipment. The sum of such items is substantially fixed and must be apportioned over the amount of magnesium made in the furnace in a given time. Thus, for example, the cost of the aluminum carbide-aluminum reducing agent is, per pound, about equal to the cost of the well known reducing agent calcium carbide but, per pound of reducing material, the aluminum carbide-aluminum is about three times as efficient in reducing the oxidic magnesium ore, and thus when this invention is used, furnace equipment of given capacity produces about three times as much magnesium with consequent lowered cost.

A comparison between processes using ferrosilicon as the reducing agent and processes operated in accordance with this invention is contained in the following tabulation of results obtained in operations conducted under comparative conditions:

	Run		
	A	B	C
Reducing agent	Ferrosilicon containing 75% by weight of silicon.	Aluminum carbide-aluminum containing 38.73% Al_4C_3 and 40.98% Al balance impurities.	Aluminum carbide-aluminum containing 38.73% Al_4C_3 and 40.98% Al balance impurities.
Magnesium ore, calcined	Dolomite	Dolomite	Magnesite.
MgO content of the ore	40%	40%	90%
Relation MgO to reducing constituent in mix.	26% excess	26% excess	Stoichiometric.
Additional effective compound	5% CaF_2	5% CaF_2	5% $CaCl_2$
Temperature °C.	1160	1100	1100.
Time of reaction hours	8	3	3.
Percentage yield of total available Mg.	75	92.1	85.9.
Pounds of Mg produced per pound of charge.	0.1195	0.1406	0.2820.
Kwh required to produce sufficient reducing agent to reduce a pound Mg.	4.12	3.33	3.66.
Relative magnesium production per day per furnace unit.	1	2.3	4.7.

The conclusions just stated on the basis of the tabulated results are representative of the comparative results which are obtained by varying the various factors in the practice of my invention. Thus in the preferred practice of my invention, and in the form which gives highest performance at lowest operating cost, the reaction should take place at the lowest temperature consistent with good results—usually about 1100° C. in the presence of an excess of magnesium oxide over that required to combine with the aluminum carbide and aluminum in the reduction agent—usually an excess of 10 to 50 per cent. by weight, and in the presence of about 2 to 15 per cent. by weight of the reaction mass of at least one chloride or fluoride of the class consisting of magnesium and the alkaline earth metals and, preferably, in the presence of the following:

Mixture of chlorides and fluorides and, preferably, the double salt $MgF_2 \cdot MgCl_2$.

Chlorides—preferably $CaCl_2$.

Mixtures of fluorides and chlorides and, preferably, the double compound $MgF_2 \cdot MgCl_2$.

Alkaline earth metal fluorides and specifically calcium fluoride.

Magnesium fluoride.

The advantages of this invention are best reflected in the efficiency of the methods of the invention. In the high temperature reduction of oxidic magnesium ore the limiting factor of cost is, in final analysis, connected more with the cost of furnace operation than with the relative cost of the materials processed. The greater part of the total cost of processing is composed of such items as labor, supervision, fuel, power

From these figures it will be noted that the furnace unit used is two to four times as efficient when aluminum carbide-aluminum mixtures are used as the reducing agent. A feature of this comparison is the fact that such results are obtained at operating temperatures 50° centigrade lower. This lower temperature is significant because it is directly reflected in reduced deterioration of equipment and, consequently, reduced cost. Moreover it will be noted that these results are obtained with reduced power costs (in the present instance 12 to 23 per cent. less). While the amount of aluminum in the aluminum carbide-aluminum mixture is not critical, practical considerations limit the aluminum content to not more than about 85 per cent. of the total aluminum carbide-aluminum content of the mixture.

Having thus described and explained my invention, I claim:

1. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use of a reducing agent containing aluminum carbide.

2. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as a reducing agent of the product of the partial reduction of aluminous ore with carbon, said product containing aluminum carbide and aluminum, the aluminum being not in excess of 85 per cent. by weight of the total content of aluminum carbide and aluminum.

3. In the process of producing magnesium by

7

the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as a reducing agent of the product of the partial reduction of aluminous ore with carbon, said product containing aluminum carbide and aluminum, the aluminum being not in excess of 85 per cent. by weight of aluminum carbide-aluminum content, and mixing said ore with said agent in such proportions that the magnesium oxide content is present in excess of the amount theoretically necessary to react with all aluminum carbide and aluminum in said agent.

4. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as reducing agent of a mixture of aluminum carbide and aluminum and mixing with the reaction mass containing said ore and reducing agent, 2 to 15 per cent. by weight, of the total weight of said mass, of at least one compound selected from the class consisting of the fluorides and chlorides of magnesium and the alkaline earth metals.

5. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as reducing agent of a mixture of aluminum carbide

8

and aluminum and mixing with the reaction mass containing said ore and reducing agent, 2 to 15 per cent. by weight, of the total weight of said mass, of the compound $MgF_2 \cdot MgCl_2$.

6. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as reducing agent of a mixture of aluminum carbide and aluminum and mixing with the reaction mass containing said ore and reducing agent, 2 to 15 per cent. by weight, of the total weight of said mass, of the compound $CaCl_2$.

7. In the process of producing magnesium by the thermal reduction of oxidic magnesium ore at temperatures above the melting point of magnesium, the improvement consisting in the use as reducing agent of a mixture of aluminum carbide and aluminum and mixing with the reaction mass containing said ore and reducing agent, 2 to 15 per cent. by weight, of the total weight of said mass, of a mixture of magnesium fluoride and calcium fluoride.

8. The improved process of claim 4 characterized by the fact that the magnesium oxide content of the charge is in excess of that theoretically required to react with all of the aluminum carbide and aluminum in said charge.

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