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PRODUCTION OF MAGNESIUM FROM SILICATES

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This invention relates to the extraction of Mg metal directly from Mg bearing silicate rocks, particularly in a molten bath of fluxing reagents through the chemistry of base exchange which is assisted by electric current at temperatures below 1000° C.

Specifically it employs a mixture of chlorides and fluorides with the salts of elements such as Cs, Li, K, Na, Sr or Ca. These elements are more electropositive than Mg and therefore are capable of replacing Mg in the silicate structure, thus releasing Mg in the metal form.

The high price and low consumption of Mg metal reflect the current high cost of Mg metal production. Electrolysis of $MgCl_2$, $2H_2O$, which is used at present, produces Mg metal from sea water or brines and requires several concentration and purification steps. Another process, employing ferrosilicon, produces Mg metal in a vapor state from MgO at a higher temperature of 1400° C. necessitating auxiliary equipment to prevent a reversal of reaction as Mg in a vapor state is highly reactive and hazardous.

It is an object of the present invention to produce metallic magnesium and its alloys directly from silicate ores.

It is a further object of this invention to produce magnesium and its alloys directly from magnesium bearing silicate ores without prior treatment other than calcining. Another object is to produce magnesium and magnesium alloys from magnesium bearing silicate ores by direct electrolysis of such ores in a fused bath. Still another object is to separate and recover metallic magnesium from its silicate ores by a treatment including base exchange with fluxing agents containing one or more elements more electro-positive than magnesium. These and other objects will become apparent from the following description.

The present invention relates to a process for the production of metallic Mg from silicate ores which have melting temperatures of 1500° C. to 1900° C. in contrast with MgO—magnesia—which has a melting temperature of 2500° C. This process operates at temperatures of 575° C. to 980° C. which are much lower than the vaporization point of 1107° C. of Mg metal; it requires no pre-processing to remove impurities; or to convert the ore to chloride or other states for processing; it takes very little current; it operates without pressure and in inert atmosphere. Any impurities that end up in the metallic magnesium are removed when Mg alloys are made to any desired specifications in one continuous melting process from raw material to the finished alloy.

The raw material suitable for the new process is abundant and occurs in many unaltered and altered basic rocks such as dunite, norite, peridotite, serpentine and others. Among unaltered Mg bearing silicate minerals are: Olivine—(Mg, Fe)SiO_4, forsterite—Mg_2SiO_4, enstatite—$MgSiO_3$, hypersthene or anthophylite—(Mg, Fe)SiO_3, pyroxenes, amphiboles, asbestos, actinolite, diopsite, and tremolite which carry, in addition to Mg, varied amounts of Fe, Ca, and Al. Among the altered Mg bearing minerals are serpentine—$H_4Mg_3Si_2O_9$, talc—$H_2Mg_3Si_4O_{12}$, or soapstone; chlorite—

$$(Mg, Fe, Al)_6(SiAl)_4 10(H_2O)$$

meerschaum—$H_2Mg_2Si_3O_{10}$, and several other minerals of more complex composition.

For comparison, the amount of magnesium metal present in each basic raw material is shown in the following table:

Sea water ... 0.78%, mostly in form of hydrated magnesium chloride.
Magnesite ... 28.8%, $MgCO_3$, Mg carbonate.
Dolomite ... 13.2% $CaCO_3$, $MgCO_3$, a double carbonate.
Olivine ... 28.8% $MgFeSiO_4$, unaltered Mg silicate.
Serpentine ... 25.2% in form of hydrated Mg silicate.

The process is particularly adaptable to the last two minerals with higher Mg content, namely: Olivine and serpentine.

A generalized formula of the Mg silicate can be written as: $(Ca, Na)_2(Mg, Fe, Al)(Si, Al)_2(O, OH)_7$ in which the first two bracketed sets of elements constitute cations (positively charged ions) and the last two brackets the anions (negatively charged ions). By substitution, addition, or withdrawal of elements, in the above formula various silicates can be made. The simplest formula of a silicate of Mg can be represented by $MgSiO_3$ in which Mg is a positive cation and SiO_3 is a negative anion. In the center of all silicate structures is a divalent silicon Si^{++} surrounded by four oxygen ions O^{2-} in a tetrahedral coordination. This can be written as an SiO_4 grouping. Magnesium is characterized by its coordination in an octahedral grouping as MgO_6, found mostly in olivine, forsterite, pyroxenes, micas, etc., though occasionally it also occurs in a tetrahedral grouping MgO_4 as in spinel. The simple Mg silicate crystalline structure consists of an SiO_4 tetrahedral grouping and an MgO octahedral grouping in which every oxygen ion O^{2-} is located at the corners common to both SiO_4 and MgO_6 groupings, i.e., one valence of the central Si^{4+} cation and one valence of Mg^{2+} cation are bonded with one oxygen O^{2-} anion at every corner. Thus oxygen ions are arranged in a hexagonal pattern. Such an Mg crystalline structure can be disrupted by removal of oxygen, known as the reduction process, and/or by substituting for the divalent Mg cation more electropositive cations, such as Cs, Li, Na, K, Sr, Ca, or by Fe and Al cations. A single divalent cation or two univalent, or univalent and trivalent cations will replace Mg and form their respective silicates. Trivalent Al, being a neutral cation, can form in addition aluminate compounds in which Al appears as an anion. In a molten bath the silicates ionize or become electrically charged. In this state magnesium no longer remains an integral chemically combined part of the silicate but becomes a separate positively charged cation—Mg^{2+} carrying two positive electric charges. In order to form Mg metal it is necessary to introduce excess electrons into the system of which two electrons would neutralize the positive charge on each Mg cation and thus liberate magnesium as metal. In an ionized state cations are screened or surrounded by negatively charged anions. In order to lower the Mg cations' potential field and reduce their electron configuration so that Mg will drop out of the ionized state as metal, electron donors and electric current are introduced into the melt. Electron donors such as Cs, Li, Na, K, Sr, Ca, being higher in the electromotive series of elements than Mg, donate their electrons to the Mg cation and thus form Mg metal. Even Fe and Al, the trivalent elements, can provide electrons in an ionized state.

The condition for liberation of Mg as metal from an ionized system, by providing more electropositive electron donors and electric current, can also be expressed as the removal of oxygen from the system. Oxygen in an ionized state has great affinity for metallic cations and in neutralizing the cation's positive charges it forms oxides. Oxygen is also removed from the system by the carbon lining of the furnace in the form of CO and CO_2 which escape as gases. Oxygen can also be liberated at anode as elemental gas but recombines with metallic cations and

carbon. These reactions are not carried to the point where unstable silicon suboxide or elemental silicon are formed. The conditions necessary for the deposition of Mg metal from Mg silicate raw materials as described above are provided in a graphite or baked carbon vessel equipped with an air-tight hood, graphite cathode, and a combination of one or more fluxes with the ore in a molten state. The fluxes serve to lower the eutectic point of the mixture and to admit electron donors into the melt. It was found that two or more such fluxes in the form of chlorides and fluorides perform their dual purpose most effectively. The examples which follow attest to the great variety of possible flux combinations which can be used in this new process. A fairly inert atmosphere above the melt is self-generating by escaping gases, or can be maintained by the introduction of SO_2 gas or more inert gases.

Mg silicate rock as raw material seldom comes in a pure unaltered form. Therefore, after crushing through a 2" screen, the ore is dehydrated at about 800° C. to drive out the moisture and water of crystallization. The presence of water in any form interferes with the reactions necessary for the production of Mg metal by this process. Water is ionized into an H^+ ion and into an OH^- hydroxyl anion. The positively charged hydrogen ion, known as proton is highly penetrating due to its small ionic radius; it has a greater affinity for electrons thus forming hydrogen gas. The hydroxyl ion OH^-, also highly reactive, can destroy the silicate structure forming $Si(OH)_2$, hydrated silicate. It also can change into hydrogen and oxygen ions. At elevated temperatures a hydrogen ion can deprive ionized oxygen O^{2-} of one of its eight outer electrons, thus leaving this ionized oxygen with only seven outer electrons. In order to restore the octet shell of the oxygen ion an electron can be taken from the nearest metallic cation as illustrated by an Fe^{++} becoming Fe^{+++} cation, leaving fewer electrons available for deposition of Mg as metal.

The reactions for the production of Mg metal in the melt may be shown in a simplified way as follows:

(1) $MgSiO_3+(Ca^{2+}, Fe^{2+}, Na^+, Al^{3+})=$
Mg metal$+$(CaSiO$_3$ or other silicates)

(2) $Mg_2SiO_4=$Mg metal$+MgSiO_3=$
Mg metal$+3SiO_2+O_2O$ (gas)

In reaction 1, through base exchange or substitution Mg metal is released and silicates of other cations are formed in the slag.

In reaction 2, magnesium metal is formed by: removal of oxygen by the incidental formation of oxides of K, Na, Ca, Fe or other electron donors present in the system, by the affinity of carbon to oxygen thus forming CO and CO_2 as gases, and by the current which releases elemental oxygen as gas at the anode, leaving silica in the slag.

There are side reactions that go on in the melt; some of which may be reversible and catalytic in nature, others liberate small amounts of chlorine or fluorine which may account for larger flux consumption. These side reactions do not materially affect the two principal ones shown above, of which reaction 1 is the major, and reaction 2 the minor one.

It is understod, of course, that the foregoing equations and description are merely explanatory of what is believed to occur in the practice of my invention for purposes of illustration and that I do not intend to be limited to any particular theory in the practice of my invention.

The furnace for the production of Mg metal from Mg silicates is an electrothermal resistance furnace with external heating. The furnace is a steel trough closed at each end and lined with insulating firebrick, which in turn is covered on the two long sides only with baked carbon which serves as the cathode. An iron metal sheet is attached to the carbon for better formation of Mg metal globules which rise to the surface of the melt near the long sides of the furnace where the Mg metal is decanted or skimmed off into a separate holder in which impurities are removed and the desired alloy consistency is attained. The pouring troughs between furnace and metal holder are also totally air-tight. The furnace bottom and the short sides are not covered with carbon so as to avoid the possible oxidation of Mg metal or formation of Mg chloride in the area below the anode iron or graphite rods which are extended lengthwise through the middle of the furnace. A separate air-tight hood is provided to cover the top of the furnace with suitable portholes for the admission of fluxes, ore, for escaping gases, for electrodes, control instruments, and removal of Mg metal. At the lower portion of the furnace a tap hole is provided for draining the melt into separate containers so as to recover reusable fluxes and discharge the resultant silicate slag.

The process can be operated on the basis of an eight hour cycle for tapping the melt, and removing Mg metal every two hours. The operation is started by preheating the fluxes to form a molten bath into which dehydrated ore is fed until the desired fluidity and the formation of Mg metal is attained with the passage of current. As reaction progresses, more ore and fluxes are added. As Mg metal accumulates a sprinkling of potassium chloride flux on top of the floating Mg metal will reduce the chances of Mg loss due to possible reactions with gases. A constant agitation of the molten bath by rising gases at cathode, rising globules of Mg metal at anode and the scraping iron rod will tend to prevent stratification of fluxes and silicates into layers due to their differences in specific gravity. At the same time during the period of slag pouring such stratification will aid in recovering molten fluxes for reuse.

Due to side reactions a certain amount of Mg metal will be lost as metal or MgO on the bottom of the furnace where impurities such as iron, iron oxide, and other heavier compounds with silicates may accumulate in the form of sludge. The sludge, being heaviest, is separated from the silicates, first through the tap hole or by scraping. Then the silicates are drained through the tap hole into container and the fluxes into a different one during the pouring period. In commercial operations my process may be carried out in banks of several furnace units, if desired.

In view of the simplicity and cheapness of the process itself, and the practically inexhaustible supply of Mg silicate ore it may prove advantageous to operate at a low recovery of Mg metal in the order of 60–75%. Extraction of the last 25% would require a considerable increase in flux and current consumption reaching a point of diminishing return.

The Mg metal may contain as impurities Fe, Al, Ni, Cr, and possibly Mn. These elements may be removed in the alloying step of the Mg metal in the known manner with salts of thorium, zirconium, cerium, rare-earths and the like. In my process these materials may advantageously be partially introduced into the melt prior to the alloying step. The new process will make possible a much better crystalline structure in the Mg alloy because the currently employed several remeltings of Mg metal will be avoided. In forming Mg alloys relics of previous remelting structures of Mg tend to remain. With the new process only one melt will be required from raw ore to a finished Mg metal alloy. This will permit a greater control of metal composition and a much finer crystalline granularity of the Mg alloys. The following typical examples will illustrate the application of the new process:

Example I

A mixture consisting of 15 parts by weight of cryolite (Na_3AlF_6), 30 parts of potassium chloride (KCl) and 4 parts of calcium chloride ($CaCl_2$) was melted in the graphite crucible at a temperature of 800° C. in an enclosed furnace heated by an electric coil. Three parts

by weight of olivine rock crushed through 100 mesh and previously dehydrated was introduced into the melt. Th molten mixture was occasionally stirred with a carbon rod and in an hour temperature was gradually raised to 880° C. Two parts by weight of KCl were added toward the end of the run in order to provide a cover for molten small globules of Mg metal which accumulated on top of the melt. These Mg metal globules were attacked by the oxygen of the air and formed MgO with brilliant flashes. The ore to fluxes ratio was about 6% and the recovery was estimated to be 55%.

Example II

A mixture of 15 parts by weight of cryolite, 30 parts of KCl, and 2 parts of sodium chloride (NaCl) was used as in Example I.

A mixture of 3 parts by weight of minus 100 mesh previously dehydrated olivine rock was made with fluxes and placed in the graphite crucible at 900° C. When the melt was formed an iron rod as anode was inserted into the melt and 3 ampere D.C. current was applied at 4½ volts for 5 minutes. The run lasted for 45 minutes during which the temperature was raised to 980° C. and the melt was stirred occasionally with the carbon rod. Minute globules of Mg metal appeared on the surface of the melt and burned out with brilliant flashes when the furnace was opened. The ore to fluxes ratio was about 5% and the recovery of metal was estimated to be 45%.

Example III

A mixture of 6 parts by weight of cryolite, 30 parts of KCl, 2 parts of $CaCl_2$ and one part of lithium chloride (LiCl) was made with 3 parts of dehydrated serpentine rock ground through 100 mesh. This mixture was introduced into the graphite crucible at 850° C. temperature. When the melt was formed D.C. current of 2 amperes at 2½ volts was applied with an iron rod as anode for 15 minutes. During the 35 minute run of this test the temperature was raised to 915° C. with occasional stirring by the carbon rod. At the end of the run 10 parts of KCl were added to the melt to prevent oxidation of Mg metal which was formed on top of the melt. The ore to fluxes ratio was about 8% and the Mg metal recovery estimated at 70%.

Example IV

A mixture of 11¼ parts of cryolite, 22½ parts of KCl and 2¼ parts of LiCl was prepared and placed into a graphite crucible at about 850° C. Three parts of previously dehydrated olivine ore ground through 20 mesh was added to the mix and occasionally stirred with the carbon rod for 40 minutes during which time the temperature was raised from 895° C. to 910° C. With added precautions to exclude air and a cover of 5 parts of KCl on top of the melt where almost continuously bright flashes took place due to oxidizing of Mg metal, many globules of Mg metal were saved for tests. The ore to fluxes ratio was about 8% and the recovery of Mg metal is estimated at 80%.

It will be noted from the description of these typical examples that various consistencies of reagents can carry the reaction to the desired completion. The reagents introduce metallic elements into the melt in larger quantities than those required for stoichiometric replacement of Mg from the silicate. The use of D.C. current as a supplementary means of promoting the reactions in the melt was made at an estimated current density of up to 2 amperes per square inch. It was also demonstrated that low current density, though assisting the principal reactions to take place, does not enhance other metallic elements to appear with Mg metal as impurities. Though the reagents mentioned can be used to effect the reactions for Mg metal production in various combinations, the examples show only a few typical variations and are not limiting.

Among the fluxing reagents, some of which serve the dual purpose of lowering the temperature of the melt and providing cations for the replacement of Mg cations, are: KCl, $MgCl_2$, NaCl, $CaCl_2$, $BaCl_2$, LiCl, Na_3AlF_6, CaF_2, KF, NaF, LiF.

With some ores, the reaction may be promoted by the addition of $NaSiO_3$, or elemental Zn, Fe, or C. As indicated above, the addition of Mn, Ga, Zr, Th, and the rare earths, in the form of oxides or salts, to the melt serves to reduce contamination of the molten magnesium with metals such as Fe, Al, Ni, and Cr.

Power consumption in my process is relatively low, being in the order of 2–5 kwh. per pound of metal produced. The amount of ore, by weight, may be up to 25% of the amount of flux in the bath, the amount, preferably, is in the order of from 3–8%.

Many other specific applications and modifications of the invention will be apparent to those skilled in the art from a consideration of the foregoing description and examples and it is understood, therefore, that the invention is not limited to any such details except as defined in the following claims.

What I claim is:

1. A process for producing magnesium from magnesium-bearing silicate ores which comprises forming a melt from a member of the group consisting of Na_3AlF_6, the halides of Li, Na, K, Cs, Ba, Sr, and Ca and mixtures thereof, said melt having a melting point below about 1000° C., adding to said melt a substantially dehydrated silicate of magnesium, passing direct current at a low current density through the resulting reaction mixture and recovering magnesium metal from said reaction mixture.

2. A process according to claim 1 in which the reaction mixture is maintained at a temperature above the melting point of magnesium.

3. A process according to claim 1 in which the reaction mixture is in contact with carbon.

4. A process according to claim 1 in which a compound from the group consisting of the oxides and salts of Mn, Ga, Zr, Th, and the rare earths is added to the reaction mixture prior to recovery of magnesium metal therefrom.

5. A method for producing magnesium from magnesium-bearing silicate ores which comprises forming a melt from a member of the group consisting of Na_3AlF_6, the halides of Li, Na, K, Cs, Ba, Sr, and Ca, and mixtures thereof, said melt having a melting point below about 1000° C., adding to said melt a substantially dehydrated silicate of magnesium, maintaining the resultant reaction mixture at a temperature above the melting point of magnesium but below about 1000° C. in contact with a member from the group consisting of elemental Zn, Fe, and C, and recovering metallic magnesium in molten form from the reaction mixture.

6. A method for producing magnesium as set forth in claim 5 in which direct current at low current density is passed through the reaction mixture.

7. A method for producing magnesium as set forth in claim 5 in which a member from the group consisting of the oxides and salts of Mn, Ga, Zr, Th, and the rare earths is added to the reaction mixture prior to recovery of magnesium metal.

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