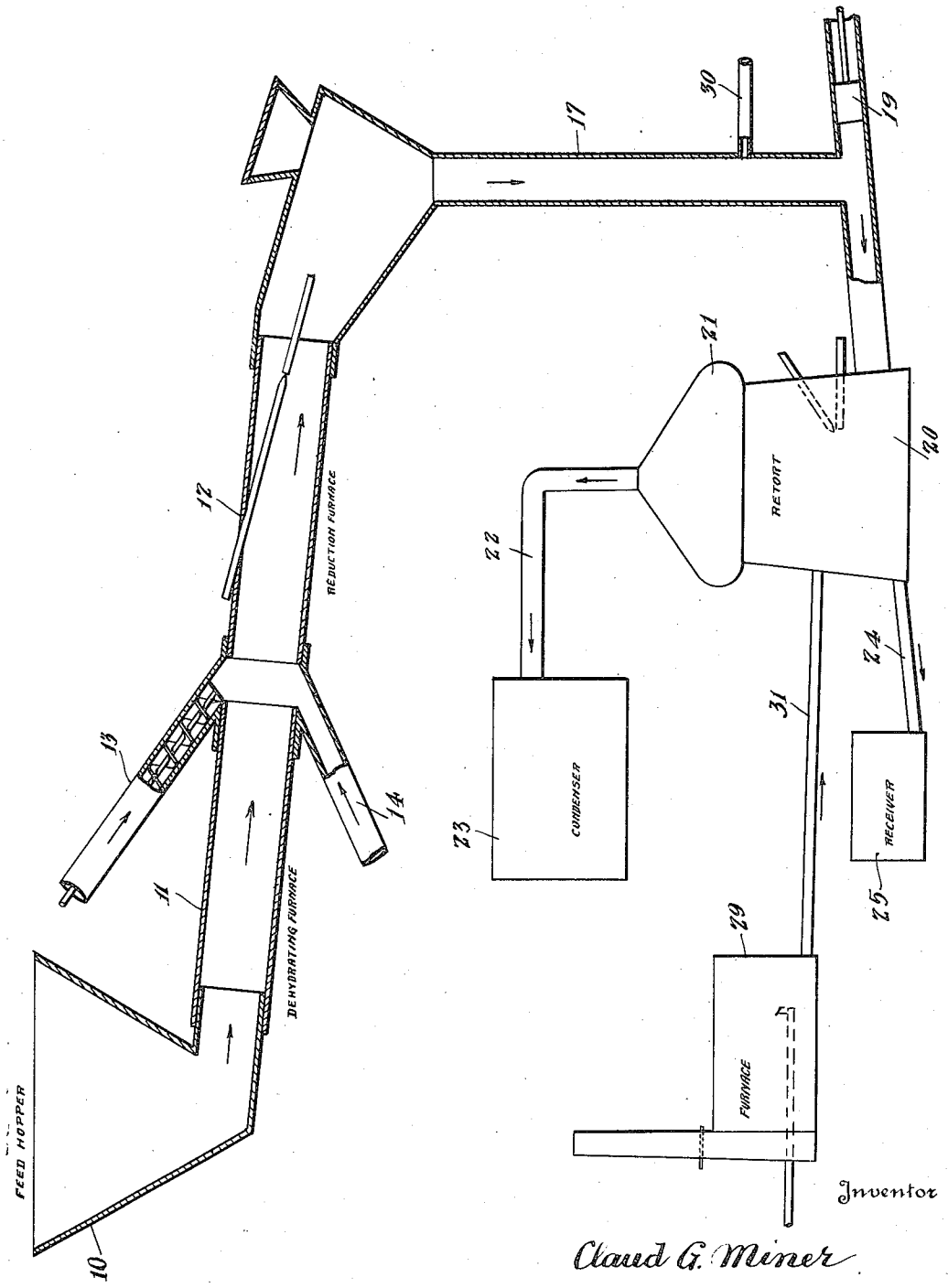
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PROCESS FOR THE PRODUCTION OF METALLIC MAGNESIUM AND FIXED NITROGEN

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PROCESS FOR THE PRODUCTION OF METALLIC MAGNESIUM AND FIXED NITROGEN.

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This invention relates to a process for the production of metallic magnesium and for the fixation of nitrogen, said process involving generally first the treatment of magnesium-bearing ores for the production of intermediate magnesium nitrogen compounds, and second the treatment of the magnesium nitrogen compound or the material containing it with a metathesis agent, whereby metallic magnesium is liberated and a nitrogen compound of the metathesis agent is formed.

At the present time it is common practice to produce metallic magnesium by electrolytic action upon fused magnesium chloride using alkali metal chlorides as electrolytes or by electrolytic action upon magnesium oxide using certain fluorides as electrolytes. But magnesium chloride and magnesium oxide have relatively high heats of formation and do not lend themselves to a cheap and practical process for the production of metallic magnesium. An object of the present invention therefore is the preparation of metallic magnesium from compounds thereof having a lower heat of formation than the chloride and oxide. I have found that by treating magnesium-nitrogen compounds with metathesis agents at comparatively low temperatures metallic magnesium is liberated in vapor form and nitrogen compounds of the metathesis agent having a considerable commercial value are produced.

The magnesium nitrogen compounds such as magnesium nitrid and carbonitrid (designated cyanamid by some authorities) may be treated with a variety of metathesis agents under a variety of different temperature and atmospheric conditions. For example, magnesium-bearing ores, such as magnesite, dolomite, brucite, and the like, may be reduced and treated to form magnesium nitrid or carbonitrid, after which the product may be brought into intimate contact with a metathesis agent such as aluminum, boron, chromium, molybdenum, silicon, titanium, tungsten, uranium, vanadium, calcium, barium or combinations thereof or ferro alloys thereof. Any of these agents will act to liberate metallic magnesium from the nitrid or carbonitrid at a temperature in excess of 1120° C., this being the vaporization temperature of magnesium, with the simultaneous formation of a nitrogen compound of the agent having a higher vaporization or boiling temperature than the magnesium. The preferred metathesis agents are 75 to 90% ferro-silicon alloys and 60 to 90% aluminum-ferro-silicon alloys.

The drawing illustrates diagramatically one form of apparatus in which the process embodying this invention may be carried out.

Referring to the drawing, 11 indicates a rotary furnace into which magnesite or other magnesium-bearing ore previously reduced to a finely divided state is fed from the feed hopper 10. When the ore has been partially or completely dehydrated and calcined it is delivered or allowed to pass into the rotary furnace 12. Furnaces 11 and 12 are set at a slight inclination so that the ore will pass slowly therethrough by gravity. The lower end of the furnace 12 is heated to between 1000° C. and 1700° C., for instance by electrical heating means incorporated in the construction of the furnace. In the furnace 11 the ore is heated to a temperature of about 1500° C. Interposed between the furnaces 11 and 12 are carbonaceous feed device 13 and an air feed pipe 14. Carbonaceous material, preferably pulverized coke or coal, is fed through the device 13 in such quantities as to bring about the reduction of the magnesium oxide content of the ore within the furnace. Air is supplied through the feed pipe 14 to sustain, promote, increase and regulate the combustion of residual material in the calcining furnace and the gases passing from the furnace 12 in which nitrogen fixation takes place. In case magnesium nitrid is desired, the temperature of the furnace 12 is maintained at 1500 to 1700° C., nitrogen or producer gas rich in nitrogen being supplied at the lower end of the furnace 12 through the pipe 30. At a temperature of 1500 to 1700° C. magnesium oxide mixed with carbon in an atmosphere of nitrogen or producer gas rich in nitrogen is converted to magnesium nitrid in accordance with the following reaction equation:

$$3\,MgO+3C+N_2=Mg_3N_2+3\,CO$$

The furnace product containing magnesium nitrid drops through the chute 17 and is

forced by the ram 19 into the electrically heated retort 20—21, where it is treated with the metathesis agent, the metallic magnesium vapors so formed passing through the conduit 22 and collecting in the condenser 23. A 75 to 90% ferro-silicon alloy is the preferred metathesis agent. It may be prepared on the spot in the furnace 29 and delivered directly in molten form into the retort 20 through the pipe 31. Ferro-silicon is not only inexpensive but the iron content thereof assists the reaction. When using ferro-silicon and a reaction temperature at or slightly above the melting point thereof the reaction mixture remains in molten condition, thus facilitating the removal from the retort of the silicon nitrid formed, and moreover the formation of a skin of silicon nitrid upon the magnesium nitrid as when silicon is used as the metathesis agent, is prevented and the completion of the reaction thus facilitated. The magnesium vapors generated in the retort 20 are collected in the condenser 23 from which magnesium may be run off in pig form. The reaction residue containing silicon nitrid is discharged from the retort through the conduit 24 into a receptacle 25. Silicon nitride is an excellent fertilizer, claimed by some authorities to be superior to calcium cynamid.

The foregoing procedure is continuous and eliminates the difficulties heretofore encountered in the manufacture of magnesium.

Instead of forming magnesium nitrid as described above the magnesium content of the ore may first be converted to magnesium carbonitrid from which magnesium is liberated by the action of a suitable metathesis agent with the formation of the carbonitrid thereof. For this purpose the procedure may be as follows:

The magnesium-bearing ore is calcined in the rotary furnace 11 up to a temperature of 1200–1500° C. and then passes into the furnace 12 which is maintained at a temperature of 1000 to 1500° C. Nitrogen and hydrocarbons capable of reacting therewith in the presence of a high tension arc to form hydrocyanic acid such as acetylene, natural gas, methane, crude oil vapors, etc., or nitrogen, hydrogen and carbonaceous material are injected into the lower end of the furnace 12 and a high tension arc is arranged and maintained in the lower part of the furnace in such a way that the material injected will be in contact with it for the longest possible time. In this case it is not necessary to feed carbonaceous material at 13 as in the method of making magnesium nitrid described above. Under the conditions stated the magnesium oxide content of the ore and the nitrogen and hydrocarbon or nitrogen, hydrogen and carbonaceous material react forming magnesium carbonitrid. Theoretically the nitrogen and hydrocarbon or nitrogen, hydrogen and carbon combine in the presence of the high tension arc forming HCN which then reacts with the magnesium oxid, forming the carbonitrid according to the following reaction equation:

$$MgO+2HCN=H_2+CO+MgCN_2$$

The furnace product containing the magnesium carbonitrid then passes to the retort 20—21 where it is treated with a metathesis agent for the liberation of metallic magnesium vapor and the formation of the carbonitrid of the metathesis agent. A variety of metathes's agents may be employed, but in this case an aluminum-ferro-silicon alloy containing 60% to 90% of aluminum is preferred. Such an alloy may be prepared on the spot in the furnace 29 by the direct reduction of bauxite or other aluminous material, in accordance with the method worked out by Minot of France, and delivered directly into the retort. The reaction between the magnesium cyanamid and the aluminum-ferro-silicon alloy is carried out preferably at a temperature of about 1000° C. under partial vacuum but may be carried out at atmospheric pressure using a temperature of say 1200 to 1500° C. The magnesium content of the magnesium carbonitrid is liberated, vaporized and recovered as described above, while the aluminum content of the alloy is converted to cyanamid and remains in the retort with the silicon and iron content of the alloy. The temperature at which the metathesis is carried out should not exceed about 1500° C., as at 1520° C. aluminum nitrid is formed instead of aluminum cyanamid.

The aluminum cyanamid formed in accordance with the foregoing procedure may be converted to aluminum chloride with the production of sodium cyanide by heating it with sodium chloride at a temperature of 800 to 900° C.

Instead of the aluminum-ferro-silicon alloy referred to in the foregoing example other metathesis agents may be used for the conversion of the magnesium cyanamid, among which may be mentioned ferro-titanium running about 75% titanium and ferro-silicon running from about 75% to about 90% of silicon. The reaction is best carried out at a temperature sufficiently high to maintain the metathesis agent, in case ferro alloys are used, in molten form but in any case the reaction must be carried out at a temperature sufficiently high to vaporize the magnesium, i. e. 1120° C. at atmospheric pressure or at a lower temperature under reduced pressure.

It is naturally possible for one skilled in the art to vary the details of procedure

described above as well as the proportions of ingredients, temperatures and other conditions without departing from my invention, the scope of which is indicated in the appended claims.

Claims:

1. Process of preparing metallic magnesium which comprises reacting upon a compound of magnesium having a heat of formation less than that of magnesium oxid with an agent capable of liberating magnesium therefrom.

2. Process of preparing metallic magnesium which comprises reacting upon a compound of magnesium having a heat of formation less than that of magnesium oxid with an agent capable of liberating magnesium therefrom at a temperature of at least 1120° C.

3. Process of preparing metallic magnesium which comprises reacting upon a compound of magnesium having a heat of formation less than that of magnesium oxid with an agent capable of liberating magnesium therefrom at an elevated temperature under a pressure less than atmospheric pressure.

4. Process of preparing metallic magnesium which comprises reacting upon a compound of magnesium having a heat of formation less than that of magnesium oxid with an agent capable of liberating magnesium therefrom and of uniting with the other elements thereof to form a compound having a vaporizing temperature above that of metallic magnesium.

5. Process of preparing metallic magnesium which comprises reacting upon a magnesium-nitrogen compound with an agent capable of liberating the magnesium content thereof.

6. Process of preparing metallic magnesium which comprises reacting upon a magnesium-nitrogen compound with an agent capable of liberating the magnesium content of said compound and of combining with the other elements thereof to form a compound having a higher volatilizing temperature than magnesium.

7. Process of preparing metallic magnesium which comprises reacting upon a magnesium carbonitrid with an agent capable of liberating the magnesium content thereof.

8. Process of preparing metallic magnesium which comprises reacting upon a magnesium carbonitrid with an agent capable of liberating the magnesium content thereof at a temperature and pressure capable of volatilizing the liberated magnesium.

9. Process of preparing metallic magnesium which comprises reacting upon a magnesium carbonitrid with an agent capable of uniting with the carbonitrid radical to form a compound having a higher volatilizing temperature than magnesium.

10. Process of preparing metallic magnesium from magnesium-bearing ores which comprises converting the magnesium content of the ore to a magnesium-nitrogen compound, and then heating the ore with an agent capable of liberating the magnesium content of said magnesium-nitrogen compound.

11. Process of preparing metallic magnesium from a magnesium-bearing ore which comprises converting the magnesium content of the ore to a magnesium-nitrogen compound and then heating the ore with an agent capable of liberating the magnesium from said compound and of uniting with the other elements thereof to form a nitrogen compound of said agent having a volatilizing temperature above that of magnesium.

12. Process of preparing metallic magnesium from a magnesium-bearing ore, which comprises converting the magnesium content of the ore to a compound having a heat of formation less than that of magnesium oxid and treating the ore with an agent capable of liberating magnesium from said compound.

13. Process of preparing metallic magnesium from magnesium oxid, which comprises converting the magnesium oxid to a compound having a lower heat of formation than the oxid and treating the compound at an elevated temperature with an agent capable of liberating magnesium therefrom.

14. Process of preparing metallic magnesium which comprises calcining a magnesium-bearing ore to form magnesium oxid, treating said oxide with a carbonaceous material in the presence of nitrogen at an elevated temperature, and treating the resulting material with a metathesis agent capable of liberating magnesium from magnesium nitrid.

15. Process of preparing metallic magnesium which comprises calcining a magnesium-bearing ore to form magnesium oxid, subjecting said magnesium oxid at an elevated temperature to an atmosphere of gases capable of forming hydrocyanic acid in the presence of a high tension arc, and treating the resulting material with a metathesis agent capable of liberating magnesium from magnesium-carbon-nitrogen compounds.

16. Process of preparing metallic magnesium which comprises calcining a magnesium-bearing ore to form magnesium oxid, subjecting said magnesium oxid at an elevated temperature to an atmosphere containing nitrogen and a hydrocarbon in the presence of a high tension arc, and treating the resulting material with a metathesis agent capable of liberating magnesium from magnesium-carbon-nitrogen compounds.

17. Process of preparing metaille magnesium which comprises subjecting mag-

nesium oxide at an elevated temperature to an atmosphere containing about 20 parts of methane, 10 parts of hydrogen and 70 parts of nitrogen in the presence of a high tension arc, and treating the resulting magnesium-carbon-nitrogen compound with a metathesis agent capable of liberating the magnesium from said compound.

18. Process of preparing metallic magnesium which comprises subjecting magnesium oxid at a temperature of 1000–1500° C. to an atmosphere containing a hydrocarbon and nitrogen in the presence of a high tension arc, and treating the resulting magnesium-carbon-nitrogen compound with an aluminum-ferro-silicon alloy containing 60–90 percent of aluminum at a temperature in excess of 1120° C.

19. Process of preparing metallic magnesium which comprises subjecting magnesium oxid at a temperature of about 1000–1500° C. to an atmosphere containing a hydrocarbon and nitrogen capable of forming hydrocyanic acid in the presence of a high tension arc, and treating the resulting magnesium-carbon-nitrogen compound with a 70–90 percent ferro-silicon alloy at a temperature of about 1000–1600° C.

20. Process of preparing metallic magnesium which comprises preparing magnesium carbonitrid from a magnesium-bearing ore, and treating the magnesium carbonitrid with a ferro-silicon alloy at a temperature in excess of 1120° C.

Signed at Berkeley in the county of Alameda and State of California this 7th day of March, 1922.

CLAUDE G. MINER.