Dec. 25, 1945. T. H. McCONICA, 3D 2,391,727

METHOD OF PRODUCING MAGNESIUM

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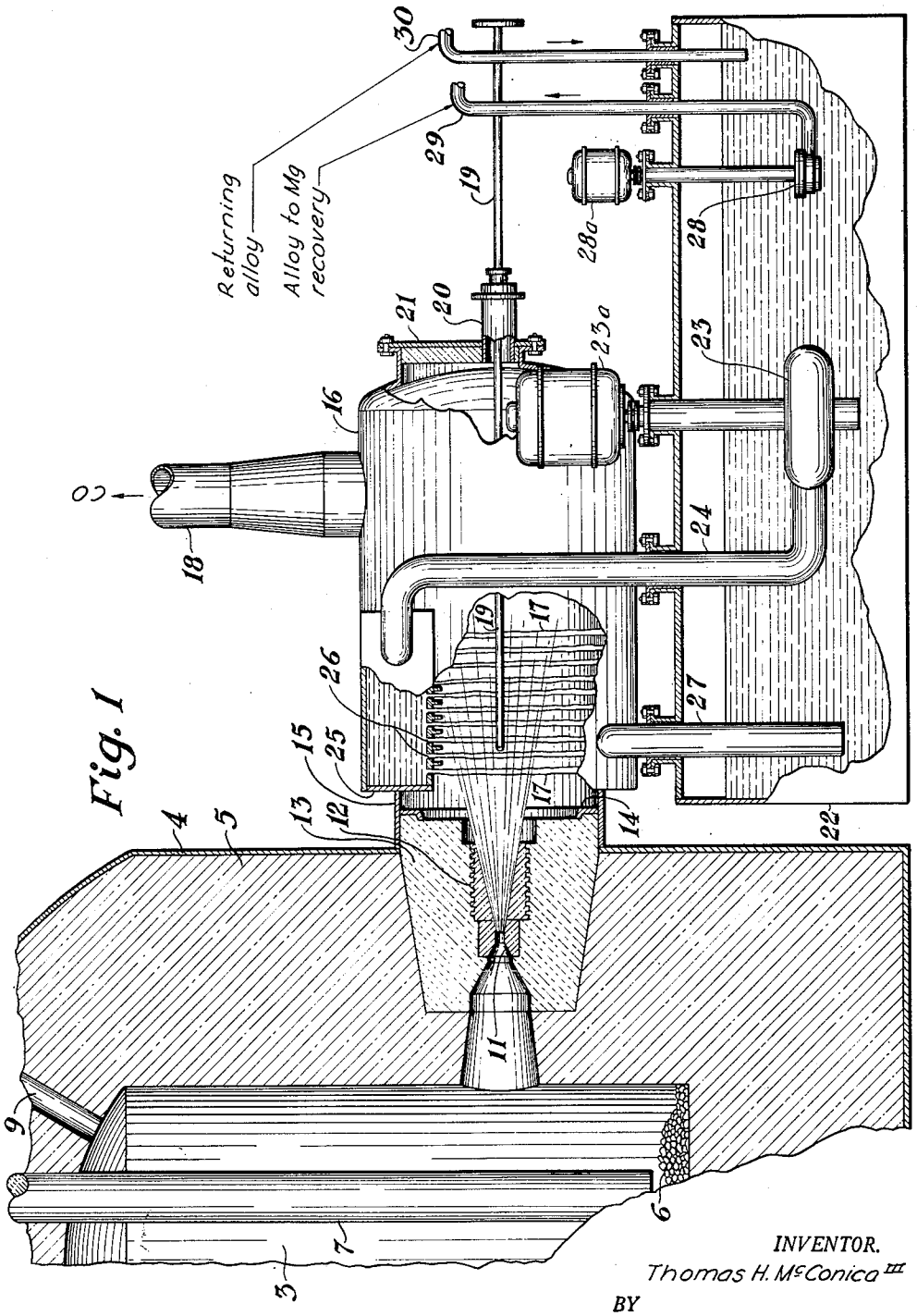


Fig. 1

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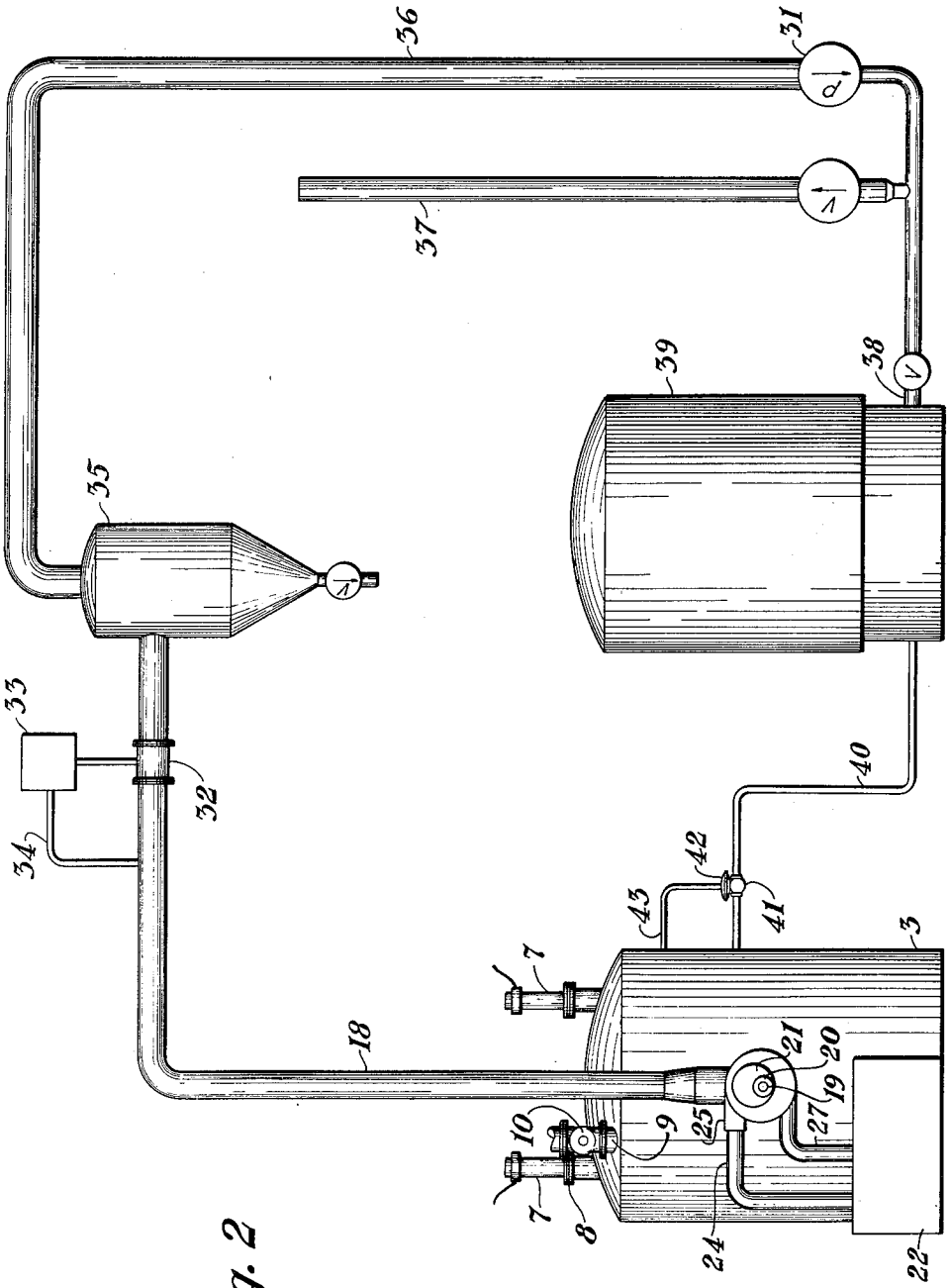


Fig. 2

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METHOD OF PRODUCING MAGNESIUM

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Application September 20, 1944, Serial No. 554,975

10 Claims. (Cl. 75—67)

This invention is concerned with the thermal production of metallic magnesium.

The interaction of solid magnesia and carbon to form a vapor mixture of magnesium and carbon monoxide is a true equilibrium process

$$MgO+C \rightleftarrows Mg+CO$$

in which, at operating temperatures, the forward and reverse reactions both proceed at appreciable rates. In consequence, it is prerequisite to the success of any carbothermic magnesium process that the operating conditions be chosen so that the rate of magnesium evolution from the charge, i. e. of the forward reaction, is great in comparison to that of the reverse reaction. At least two different ranges of temperature and pressure have been recommended in the art.

In one process, a charge mixture of magnesia and carbon is heated at atmospheric pressure to a temperature well above 1900° C. The magnesium-carbon monoxide vapor mixture thus formed is led to a condenser at atmospheric pressure and is quenched rapidly to a temperature below 650° C. to produce solid magnesium. In this method, a high rate of magnesium evolution is achieved, but great difficulty is experienced in conveying the vapor mixture to the condenser and quenching it without undue loss of magnesium by reversion to magnesia. Thus, at the operating pressure, the upper temperature of the reversion reaction, roughly 1750° C., is only slightly below the temperature of the evolving vapors. In consequence, the vapor mixture, in passing from the furnace to the condenser, is often cooled by unavoidable radiation heat loss into the range of reversion temperatures. Not only does formation of magnesia and carbon thus occur even before the quench zone is reached, but this material tends to deposit in the condenser inlets, causing mechanical plugging. In addition, within the condenser itself, in which the vapor mixture is shock-chilled through the reversion temperature range of 1750° to 650° C., difficulty is experienced in effecting the quenching with sufficient rapidity to avoid considerable further formation of magnesia and carbon. As a result of these two losses, magnesium production efficiencies exceeding 70 to 80 per cent are rarely realized.

In another known process, the charge mixture is heated under vacuum, usually at 0.001 atmosphere or less, at a temperature above 1400° C., and the evolved vapors are passed to a cooler zone at the same pressure and there chilled to condense magnesium. In this method, loss of magnesium by reversion is not excessive, but the rate of reaction must be kept undesirably low in order to avoid transport of charge particles to the condenser by entrainment in the vapor mixture. Moreover, serious practical difficulties are encountered in operating a large furnace at high vacuum. For these reasons, the process has not been satisfactory in large-scale production.

It is accordingly an object of the present invention to provide an improved carbothermal process for making magnesium in which the metal is produced at a high rate with good efficiency and in which many of the troubles of prior practice are avoided.

In the process of the invention, the magnesia-carbon charge mixture is first heated at a pressure of at least 0.5 atmosphere to a temperature sufficient to form a vapor mixture of carbon monoxide and magnesium. This mixture is then expanded to a reduced pressure between 0.1 and about 2.5 inches of mercury absolute, and is quenched at this latter pressure to a temperature below about 650° C. By operating in this manner, formation of magnesium-carbon monoxide vapor mixture may be carried out in a furnace of simple construction, at high rate and with minimum entrainment of charge particles. At the same time, the expansion of the vapors lowers the upper reversion temperature and reduces the rate of reversion so substantially that they may readily be transported to the condenser and even cooled intentionally without appreciable formation of magnesia and carbon or plugging of the vapor conduit. In addition, the quenching operation, being at drastically reduced pressure, takes place with little if any reversion of the magnesium. Exceedingly high overall recovery efficiencies may be realized.

The invention may be further explained with reference to the accompanying drawings, in which

Figure 1 illustrates, in vertical partial cross-section, one arrangement of apparatus for carrying out the expansion and quenching steps of the new process; and

Figure 2 is a side view of the furnace of Figure 1, showing auxiliary gas-circulating equipment.

In the equipment illustrated, the magnesium-carbon monoxide vapor mixture is generated in an arc furnace 3 formed of a gas-tight steel shell 4 lined with refractory carbon blocks 5 and having a hearth 6 of broken coke. The furnace is heated electrically by arcs struck between the hearth and graphite electrodes 7 which enter

through water-cooled gas-tight glands 8. Charge mixture is fed in through an upper inlet 9 provided with a variable-speed rotary lock 10.

The vapor mixture leaves the furnace through a narrow-throated expansion orifice 11 formed in a small block of highly refractory material, such as boron carbide. The diameter of the orifice is ordinarily quite small, being usually only a few inches, even for furnaces of very large size. The orifice body 11 is held by a carbon bushing 12 in a socket in a carbon thrust-block 13 secured in the furnace wall and seated on a steel ring 14 welded to the furnace shell.

The expanding vapors issuing from the orifice 11 enter a conduit 15 which leads into a gas-tight thermally insulated quench chamber 16. In this chamber, the vapor stream impinges on successive falling streams 17 of a quench liquid, in which the magnesium is shock-chilled and condensed. The non-condensable carbon monoxide is continuously exhausted through a suction stack 18.

Any solid deposit forming in the vapor orifice 11 may be poked loose by an alloy steel reamer rod 19 of diameter slightly less than that of the orifice. This rod is mounted slidably opposite the orifice in a gland 20 welded through a cover flange 21 on the end of the quench chamber.

The quench liquid, preferably a molten lead-magnesium alloy, is maintained under inert gas protection in a closed insulated reservoir 22. A portion of the quench liquid is continuously forced by a pump 23 driven by motor 23a through an insulated line 24 into a distributing box 25 formed in the top of the chamber 16 above the quench zone. This liquid falls through transverse slots 26 cut in the bottom of the box 25 in wide streams 17 having the effect of liquid sheets or curtains, and is collected in the bottom of the quench chamber and returned to the reservoir 22 through an insulated drain pipe 27. Part of the quench liquid containing condensed magnesium is withdrawn continually from the reservoir by a pump 28 driven by motor 28a and is circulated through a pipe 29 to a magnesium recovery system not shown, from which the magnesium-depleted liquid is returned for re-use by a pipe 30.

The suction in the stack 18 is created by a vacuum pump 31 and is regulated by a damper 32, which may be rotated by a position controller 33 in response to variations in quench pressure conveyed to the controller by a gauge line 34 connected into the stack. The carbon monoxide flowing through the stack 18 enters a cyclone separator 35 to remove any suspended dust before reaching the vacuum pump through a line 36.

The carbon monoxide exhausted by the vacuum pump may be vented through a valved line 37, or it may be circulated to storage through a second valved line 38 leading into a gas holder 39. From this gas holder, the carbon monoxide may be returned to the arc furnace through a connecting pipe 40 in which flow is regulated by a valve 41, this latter being adjusted by a controller 42 in response to variations in furnace pressure transmitted by a gauge line 43.

In operation of the apparatus illustrated, the arc furnace is maintained at a temperature of at least 1900° C., preferably 2000° C. or more, and a charge mixture of magnesia and carbon is admitted continually through the inlet 9, falling into the hearth 6 and rapidly evolving a vapor mixture of magnesium and carbon monoxide. The pressure in the furnace is held above about 0.5 atmosphere, either by admitting carbon monoxide from the gas holder in regulated flow through the automatically-controlled valve 41, or by adjusting the rate at which the charge mixture is fed, or by both. In addition, small flows of carbon monoxide or other protective gas are introduced into the electrode glands 8 and charge inlet 9 by means not shown to prevent entry of furnace vapors into those openings.

The quench chamber is maintained at a pressure in the range 0.1 to about 2.5 inches of mercury absolute, preferably about 0.2 to about 1.0 inch, by the action of the pump 31, the pressure being automatically regulated by damper 32 to hold the set pressure. The temperature of the quench liquid falling through the quench-chamber is controlled below 650° C. by heat-exchangers (not illustrated) in the reservoir 22. Likewise, the concentration of magnesium in the quench liquid is held roughly constant by regulating the recovery system fed by the pump 28. For example, when the quench liquid is a lead-magnesium alloy, the temperature is preferably controlled in the range 500° to 600° C. and the concentration of magnesium between 8 and 15 per cent by weight, the recovery of magnesium being conveniently carried out by boiling magnesium out of the alloy at reduced pressure, in accordance with known practice.

Under the conditions just described, the magnesium-carbon monoxide vapor mixture is evolved rapidly from the charge, and flows toward the orifice 11 at a relatively low rate, entraining few if any charge particles, and remaining at a temperature at least slightly above its upper reversion temperature until it enters the orifice. There, because of the large pressure drop, it expands with extreme velocity, entering the pipe 15 and at once assumes the pressure in the quench chamber. In this pipe, the temperature of the vapor mixture, which is still essentially that of the furnace, is far above the upper reversion temperature corresponding to the prevailing low pressure. The mixture is thus maintained under substantially non-reversionary conditions at all times until it meets the streams 17 of quench liquid. Moreover, even when the vapors are cooled into the reversion range during condensation by the quench medium, the rate of reversion is very low because of the reduced pressure. In addition, excellent intimacy of contact is obtained between the quench liquid and the vapor mixture, since the latter impinges on the flowing liquid at high velocity. As a result of these factors, the magnesium vapor is, in contrast to prior processes, quenched and condensed rapidly and effectively, without appreciable reversion to magnesia and carbon.

By virtue of the fact that the vapor mixture flowing in the pipe 15 is at a temperature far above its reversion range, it may, if desired, be cooled substantially before it reaches the quench curtains 17, thus appreciably reducing the cooling load on the quench medium. This cooling is preferably accomplished by radiation, i. e. simply by not insulating the pipe 15 completely, although positive cooling, as by injection of cold carbon monoxide, may be used.

As already stated, in the process of the invention, the pressure in the furnace may be controlled at any value above about 0.5 atmosphere. However, it is advantageous to operate with the furnace at, or even above, atmospheric pressure, since at these pressures operation of the furnace

arcs is more stable, and higher arc voltages, with resulting higher electric power factors, may be used. In addition, at pressures approaching atmospheric, the hazard of possible air leakage into the furnace is minimized.

In general, it is better to maintain furnace pressure by adding furnace charge at a high rate rather than by recirculating large volumes of carbon monoxide through the valve 41. At the higher charging rates, the partial pressures of the evolving magnesium and carbon monoxide approximate the desired total furnace pressure, and the valve 41 is then called upon to admit recycled carbon monoxide only to make up for infrequent diminution in pressure below the set minimum. Under these conditions, optimum conditions for evolution of magnesium and carbon monoxide are realized and heat losses due to recirculation of carbon monoxide are low.

In operation of the new process, the charge mixture is conveniently a briquetted mixture of magnesia and petroleum coke, in stoichiometric proportions. However, other magnesia-containing materials, such as calcined dolomite, and other forms of carbonaceous reducing agent may be used.

The quenching liquid used is preferably a substantially non-volatile molten metal absorbent miscible with magnesium, such as lead or a lead-magnesium alloy. However, other quenching liquids, including volatile metals miscible with magnesium, molten salt mixtures, and heavy oils, may be employed. Likewise, the quench step is not limited to the use of liquid media, since other shock-chilling means, such as a rotary drum condenser, are contemplated as within the invention.

It is to be understood that the foregoing description is illustrative rather than strictly limitative, and that the invention is co-extensive in scope with the following claims.

This application is a continuation-in-part of application Serial No. 423,944, filed December 22, 1941.

Attention is directed to a co-pending application, Serial No. 584,630, filed March 24, 1945 by T. H. McConica, III, et al., in which claims are asserted to the constructional details of the quench condenser, disclosed, but not claimed, in this application.

The invention claimed is:

1. In a method of producing magnesium, the steps which comprise heating a mixture of a magnesium oxide source material and a carbonaceous reducing agent at a pressure of at least about 0.5 atmosphere and at a temperature sufficient to form a vapor mixture of magnesium and carbon monoxide, expanding the vapor mixture from such pressure to a reduced pressure between 0.1 and about 2.5 inches of mercury absolute, and rapidly cooling the vapor mixture at the latter pressure to a temperature below about 650° C.

2. A process according to claim 1 in which the vapor mixture is expanded to a pressure between about 0.2 and about 1.0 inch of mercury absolute.

3. In a method of producing magnesium by the thermal reduction of magnesium oxide with carbon, the steps which comprise heating a mixture of magnesium oxide and carbon at approximately atmospheric pressure and at a temperature sufficient to form a vapor mixture of carbon monoxide and magnesium, expanding the vapor mixture from such pressure to a reduced pressure between 0.1 and about 2.5 inches of mercury absolute, and quenching the vapor mixture at the latter pressure to a temperature below about 650° C.

4. In a method of producing magnesium, the steps which comprise heating a charge mixture of magnesium oxide and carbon at a pressure of at least about 0.5 atmosphere and at a temperature sufficient to form a vapor mixture of carbon monoxide and magnesium, expanding the vapor mixture from such pressure to a reduced pressure between 0.1 and about 2.5 inches of mercury absolute, cooling the vapor mixture while at said pressure to a temperature which is not below its upper reversion temperature, and then quenching the cooled vapor mixture while still at the said reduced pressure to a temperature below about 650° C.

5. In a process of producing magnesium, the steps which comprise: heating a charge consisting essentially of magnesium oxide and carbon in a confined zone at a pressure of at least 0.5 atmosphere to a temperature sufficient to convert the charge to a vapor mixture of magnesium and carbon monoxide, expanding the mixture directly from the confined zone through a restricted orifice into a vapor conduit maintained at a reduced pressure between 0.1 and about 2.5 inches of mercury absolute, conveying the vapor mixture through said conduit to a quench zone maintained at substantially the same reduced pressure, and quenching the vapor mixture in the latter zone to a temperature below about 650° C.

6. A process according to claim 5 in which the charge mixture is heated at approximately atmospheric pressure and in which the vapor mixture is expanded to a pressure between about 0.2 and about 1.0 inch of mercury absolute.

7. A process according to claim 5 in which the pressure in the heating zone is maintained by admitting carbon monoxide thereto and controlling the rate of such admission in response to variations in the pressure in the heating zone.

8. A process according to claim 5 in which the pressure in the heating zone is maintained by regulating the rate at which the charge is fed to the heating zone so that the sum of the partial pressures of the evolving magnesium and carbon monoxide is substantially equal to the total pressure in the heating zone.

9. A process for producing magnesium which comprises heating a mixture of a magnesium oxide source material and a carbonaceous reducing agent in a confined zone at a pressure of at least about 0.5 atmosphere to a temperature sufficient to convert the charge to a vapor mixture of magnesium and carbon monoxide, expanding the mixture from the confined zone through a restricted orifice into a quench zone maintained at a reduced pressure between 0.1 and about 2.5 inches of mercury absolute and therein passing the expanded mixture into intimate contact with a substantially non-volatile molten metal absorbent miscible with magnesium and supplied at a temperature below about 650° C. to condense the magnesium vapor in the absorbent, and removing absorbent from the quench zone and recovering magnesium therefrom.

10. A process for producing magnesium which comprises: heating a furnace zone closed except for a restricted vapor outlet at a temperature of at least about 1900° C. and introducing a charge mixture of magnesium oxide and carbon into the zone at a rate sufficient to maintain the pressure of the vapor mixture of magnesium and carbon monoxide evolving from the heated charge at at least 0.5 atmosphere; expanding the evolv-

ing vapor mixture through the restricted outlet into a quench zone at a pressure between about 0.2 and about 1.0 inch of mercury absolute and therein passing the expanded vapor mixture into intimate contact with a substantially non-volatile molten metal absorbent consisting predominantly of lead and maintained at a temperature below about 650° C. to condense the magnesium vapor in the absorbent; exhausting uncondensed carbon monoxide from the quench zone at a rate sufficient to maintain the pressure in the zone within the aforesaid limits; and withdrawing the absorbent from the zone and recovering magnesium therefrom.

THOMAS H. McCONICA, III.