July 14, 1970 E. A. STAWARZ ET AL 3,520,524

PRODUCTION OF MAGNESIUM UTILIZING A TUBULAR CONDENSER

Filed Oct. 17, 1967 2 Sheets-Sheet 1

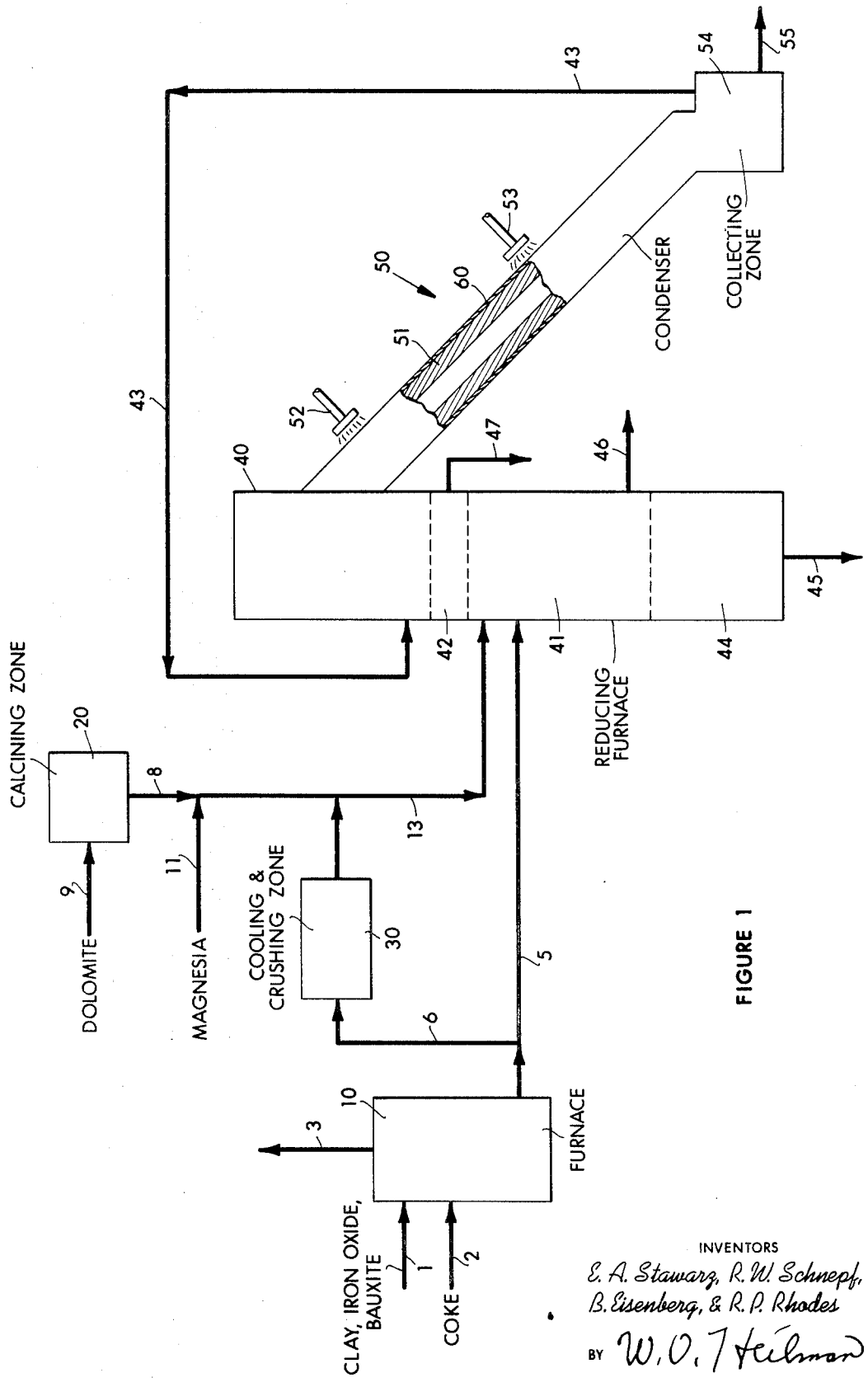


FIGURE 1

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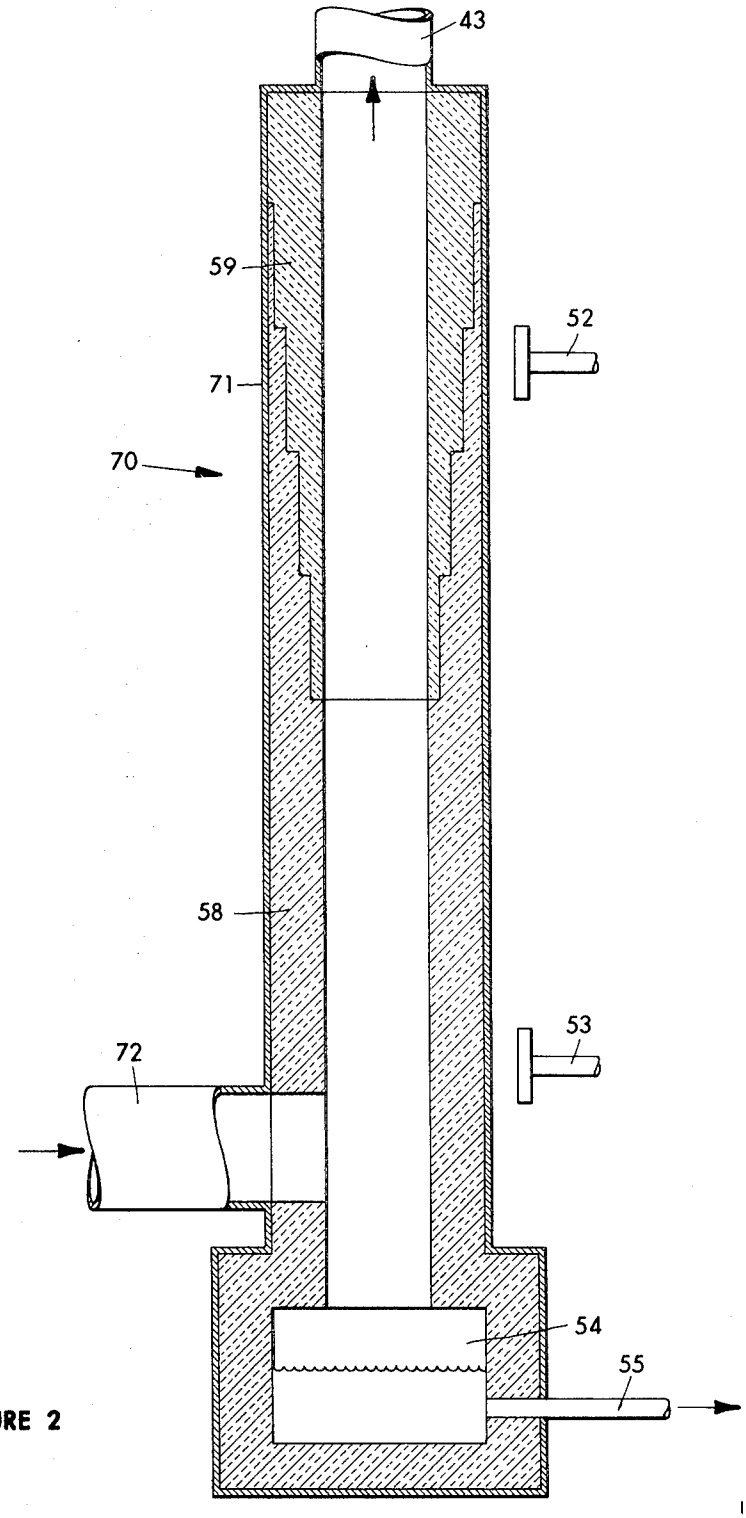


FIGURE 2

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PRODUCTION OF MAGNESIUM UTILIZING A TUBULAR CONDENSER

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U.S. Cl. 266—34 4 Claims

ABSTRACT OF THE DISCLOSURE

A thermal apparatus for the production of magnesium metal at substantially atmospheric pressure which comprises heating an alloy mixture in a reaction zone at a temperature in the range from about 2850° to 3100° F., removing a gaseous mixture of hydrogen and magnesium vapor from the reaction zone and thereafter utilizing a tubular condenser to remove and recover the magnesium as a liquid.

The present invention is broadly concerned with the production of high quality magnesium metal utilizing a thermal technique. The invention is especially concerned with the thermal treatment of a feed mixture of dolomite (CaO-MgO) and aluminum silicon (Al_2Si) utilizing an apparatus and other feed reactants wherein magnesium vapor is continuously produced. The magnesium is recovered from a gaseous mixture of magnesium and hydrogen or other inert gas by the utilization of a unique tubular condenser.

It is known in the art that the present thermal methods for the production of magnesium are slow batch operations wherein a high vacuum is required. These known thermal methods thus are not suitable for operations on a scale large enough to compete with the electrolytic cell methods for the production of magnesium. The present invention is based upon the discovery that magnesium vapor may be readily distilled and recovered and that a ferrosilicon by-product may be simultaneously produced without the use of vacuum providing the reactants and the reaction zone conditions are controlled within critical limits. In accordance with one specific adaptation of the present invention, aluminum-silicon-iron alloy is reacted with a critical mixture of calcium oxide and magnesium oxide under temperature and pressure conditions in an integrated process to produce high quality magnesium vapor and a molten slag. Hydrogen or other inert gases may also be introduced into the reaction zone and the magnesium thereafter recovered from the gaseous mixture by the utilization of a particularly designed tubular condenser.

The tubular condenser technique of the present invention may be utilized for the recovery of magnesium from a magnesium-containing vapor mixture when using wide ranges of reactants and reaction conditions in the reduction zone. However, the invention will be described utilizing particular reactants and operating conditions and may be fully understood by reference to the drawings illustrating one preferred embodiment of the same.

Referring specifically to FIG. 1, a mixture of aluminum oxide, iron oxide and silicon oxide is introduced into

alloy furnace **10** by means of line **1**. Alloy furnace **10** may comprise any suitable furnace such as a conventional electric arc furnace. The required carbon is introduced into furnace **10** by means of line **2**. Gaseous reaction products are removed from furnace **10** by means of line **3** while an aluminum-silicon-iron alloy is removed from furnace **10** by means of line **5**. The temperature in furnace **10** is maintained in the range from about 3200° F. to 4500° F., preferably about 4000° F. The pressure in alloy furnace **10** is in the range from about 0.5 to 2 atmospheres preferably about 0.9 to 1.1 atmospheres such as about 1.0 atmosphere.

The feed reactants added to furnace **10** are preferably added in amounts so as to produce an alloy comprising about 40 to 90% by weight of aluminum, about 65 to 10% by weight of silicon and about 1 to 20% by weight of iron. A preferred alloy consists of about 50% by weight of the aluminum, about 40% by weight of silicon and about 10% by weight of iron. Satisfactory reactants for feed to alloy furnace **10** are clay, bauxite, iron oxide and carbon.

The alloy removed from zone **10** by means of line **5** comprising aluminum, silicon, and iron may be passed directly in the molten state to reducing furnace **40**. This alloy, however, may be passed by means of line **6** into a cooling and crushing zone **30** and thereafter mixed with the reaction mixture of calcined dolomite and magnesia which is introduced into the system by means of line **8**.

Calcined dolomite is produced by introducing dolomite (calcium carbonate and magnesium carbonate) into calcining zone **20** by means of line **9**. The calcined dolomite produced in zone **20** and withdrawn by means of line **8**, comprises about 55 to 65% by weight of calcium oxide and about 45 to 35% by weight of magnesium oxide. Magnesia, which is substantially pure magnesium oxide (greater than about 90%), is introduced with the dolomite by means of line **11**. The amount of magnesia added by means of line **11** is such as to secure a MgO/CaO ratio in the oxide mixture fed to the reaction zone in the range of about 50/50 to 80/20 parts by weight, preferably from about 55/45 to 65/35 and, more particularly, about 60/40 parts by weight. Alternatively, a calcined magnesitic dolomite of the proper CaO/MgO ratio could be fed directly into line **8**.

If the alloy is passed to zone **30** it is withdrawn by means of line **13** mixed with the magnesia-calcium-oxide mixture and introduced into reaction furnace **40**. On the other hand, if the alloy is introduced directly into reaction zone **40**, the magnesia-calcium-oxide mixture is introduced by means of line **13**. A preferred adaptation is to introduce about 40 to 60%, such as about 50%, of the alloy directly into zone **40** by means of line **5** and to introduce the remainder mixed with the magnesium-calcium-oxide by means of line **13**.

The amount of the mixture of calcined dolomite and magnesia introduced into furnace zone **40** as compared with the amount of aluminum-silicon-iron alloy introduced into furnace zone **40** is in the range of from about 3.0 to 8.0 parts by weight per 1.0 part by weight of alloy. A preferred ratio of the mixed oxides-to-alloy is in the range of from about 4.0 to 1.0 by weight.

Reduction furnace **40** is maintained at a pressure in the range from 0.5 to 2.0 atmospheres, preferably 0.9 to 1.1 such as about 1 atmosphere. Under one preferred

method of operation, the temperature in reduction furnace **40** is maintained in the range from about 2850° F. to 3100° F., preferably about 2950° F. The slag phase **41** in reduction furnace **40** comprises aluminum oxide, calcium oxide and silicon oxide. When the reactants are introduced into slag phase **41**, they melt and form discrete particles of alloy in slag phase **41**. These discrete particles are a homogeneous metal phase of aluminum, silicon and iron.

Under these conditions the aluminum reacts with calcium oxide to form aluminum oxide in the slag and the calcium replaces the aluminum in the discrete particles of the metal phase. This latter metal phase of iron, silicon and calcium will separate, if the slag density is sufficient, to yield an upper metal phase **42**. Hydrogen is introduced into the vaporous area of reduction furnace **40** by means of line **43**. The calcium reacts with the magnesium oxide to form calcium oxide which is segregated in the slag **41** and vaporous magnesium is formed which is removed from reduction furnace **40** along with the hydrogen by means of tubular condenser **50** and recovered as hereinafter described.

Due to the fact that a portion of the calcium in phase **42** is removed by reacting with the magnesium oxide, the density of the alloy increases and a lower phase of iron and silicon **44** forms at the bottom of reaction zone **40**. Thus, a ferrosilicon phase **44** comprising from about 30–80% silicon and 70–20% iron may be withdrawn from zone **40** by means of line **45** and utilized as desired in the steel industry. The slag is removed from reduction furnace **40** by means of line **46** and handled as desired while a ferrosilicon-calcium phase may be withdrawn by means of line **47** and further handled to segregate the respective elements.

Sufficient hydrogen is introduced into the vaporous area of furnace **40** so as to maintain the pressure at about atmospheric pressure as, for example, in the range from about 0.5 to 2.0 atmospheres. In general, the vaporous mixture withdrawn by means of condenser **50** comprises about 90 to 40 volume percent of magnesium and from about 10% to 60% of hydrogen.

The temperature of the vaporous mixture entering tubular condenser **50** is in the range of from about 2000° F. to 3100° F. usually about 2600° F. As the vaporous mixture passes downwardly through tubular condenser **50** the temperature is reduced to within the range of from about 1200° F. to 1500° F., usually about 1250° F. Liquid magnesium collects in collecting zone **54** and is withdrawn by means of line **55**. Hydrogen is removed from zone **54** by means of line **43** and recycled to reduction furnace **40**.

Tubular condenser **50** comprises a single long cylindrical metal shell **60** with an internal lining **51** such as carbon or graphite whose thickness is selected to keep the shell temperature within allowable limits. Thus, direct condensation of hot metal vapors onto a bare metal surface is avoided. High heat transfer rates are achieved either by operating with a cold shell and utilizing water as a coolant which is sprayed around the periphery of the shell by means of suitable spray elements **52** and **53**. Any number or arrangement of water spray elements may be utilized. On the other hand, the shell may be operated with a hot shell and radiating the heat to the atmosphere.

A unique feature of the present invention is that liner **51** has a relatively high heat transfer rate where the metallic vapors are condensing near the top of the unit. The liner **51** at the lower end of the condenser has a relatively low heat transfer rate. This progressive change in heat transfer rate from relatively high to relatively low of liner **51** may be achieved by any suitable means. One method will be clearly described with respect to FIG. 2.

A preferred and very satisfactory condenser in accordance with the present invention is illustrated in FIG. 2 wherein upflow of the vapors is secured. The condenser is so designed that the internal temperature of the lining along its entire length is above the freezing point of the

magnesium which is secured by having a lining of very high conductivity in the lower area of the condenser which lining is adjusted so that the conductivity of the lining decreases as the vapors flow upwardly through the condenser. Here again, the relatively high heat transfer rate for the liner is at the lower end of the condenser wherein the metallic vapors are condensing. Condenser **70** comprises a carbon steel shell **71** which is internally lined in a particular manner with courses of carbon and graphite. The vapors are removed from the furnace and introduced into condenser **70** by means of line **72**. Magnesium is condensed and is collected in area **54** and withdrawn from the system by means of line **55**. Water sprays **52** and **53** are utilized to maintain the desired temperature on the condenser exterior. Uncondensed hydrogen is withdrawn by means of line **43** and recycled as described in FIG. 1.

In order to achieve the desired results as described the diameter of condenser **70** may be from about 5 feet to 8 feet as, for example, about 6 feet. The length of the condenser is from about 80–120 feet, such as about 100 feet. The interior of the condenser as, for example in area **58**, is lined with graphite bricks as, for example, with nine courses of 2-inch graphite bricks for a total thickness of about 18 inches. The lining in the upper part of the condenser contains progressively more carbon bricks having lower conductivity. For example, the lining in area **59** consists of about eight courses of 2-inch carbon bricks and one course of 2-inch graphite bricks. The lining at the top of the condenser would consist of nine courses of carbon bricks. Thus, using a condenser of this type it is possible to maintain a temperature at the bottom of the condenser in the range of from about 2500° to 3500° F., such as about 3000° F. The temperature at the top of the condenser is thus maintained in the range from about 1250° to 1500° F., such as about 1400° F.

What is claimed is:

1. Improved condenser assembly for condensing metallic vapors whereby contact between metallic vapors and the bare metal wall of said assembly is avoided which comprises, (1) means for introducing metallic vapors into said assembly, (2) means for withdrawing condensed vapors from said assembly, said assembly characterized by (3) having a metallic shell, and (4) containing a liner therein extending throughout said condenser assembly, said liner being characterized by having a relatively high heat transfer rate at the point of introduction of said metallic vapors and a relatively low heat transfer rate at the other end of said liner, the heat transfer rate progressively changing throughout said assembly, said liner being further characterized by consisting of different materials having different heat transfer rates, which materials are adjusted with respect to one another so as to secure a progressive heat transfer rate change.

2. Condenser assembly as defined by claim **1** wherein the heat transfer rate is progressively changed throughout said assembly by interchanging carbon bricks having a relatively low heat transfer rate for graphite bricks having a relatively high heat transfer rate in the respective courses of said liner.

3. Improved condenser assembly for condensing metallic vapors whereby contact between metallic vapors and the bare metal wall of said assembly is avoided which comprises, (1) means for introducing metallic vapors into one end of said assembly, (2) means for withdrawing condensed vapors from the other end of said assembly, said assembly characterized by having a (3) metallic shell and containing a liner therein extending from said one end to said other end, said assembly being further characterized by said lining having a relatively high heat transfer rate at said one end and a relatively low heat transfer rate at said other end, the heat transfer rate progressively changing throughout said assembly, said liner being further characterized by consisting of different materials having different heat transfer rates, which ma-

terials are adjusted with respect to one another so as to secure a progressive heat transfer rate change.

4. Assembly as defined by claim 3 wherein said liner at near said one end comprises a plurality of courses of carbon bricks having a relatively low heat transfer rate and said liner at near said other end comprises a plurality of courses of graphite bricks having a relatively high heat transfer rate and wherein said liner between said one end and said other end comprises courses of carbon and graphite bricks.

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