

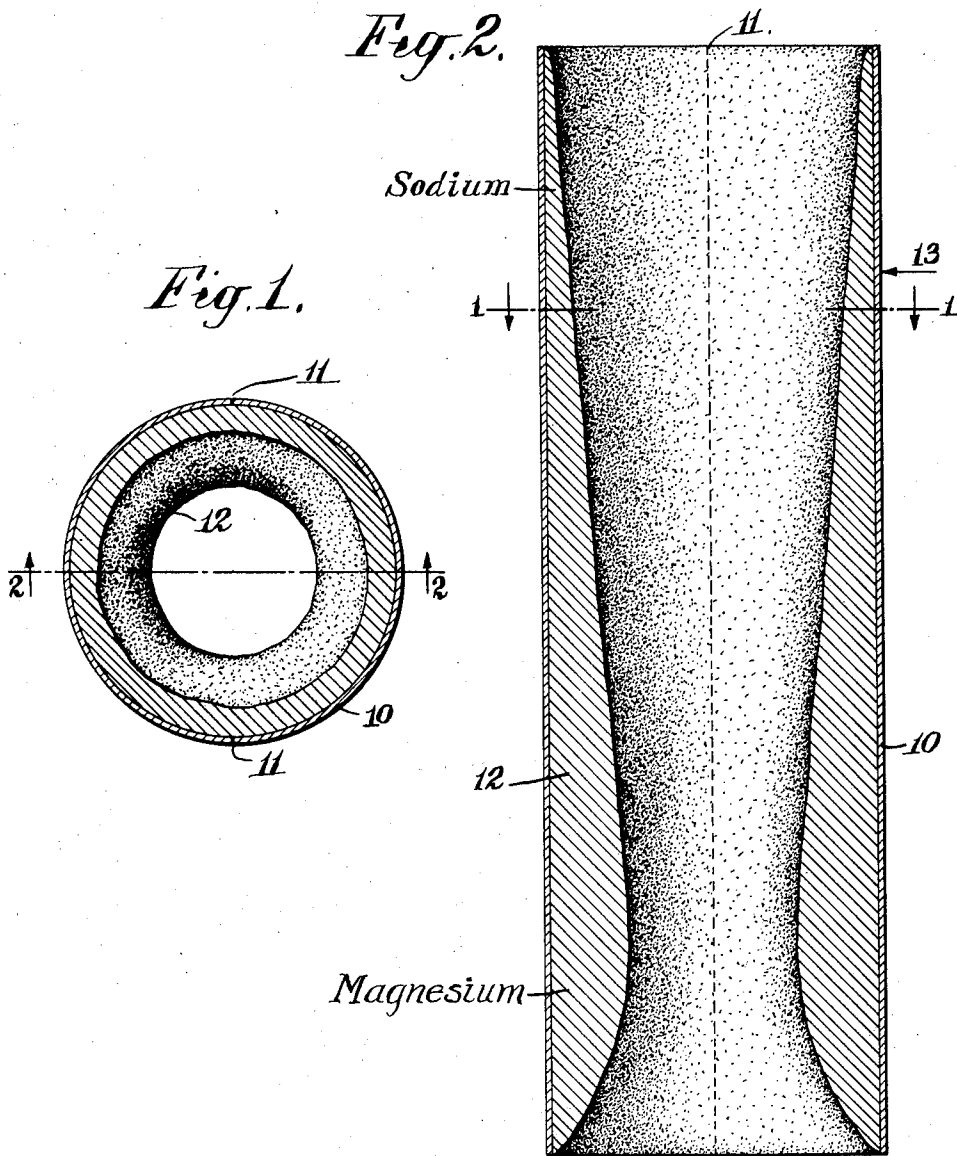
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SEPARATING VOLATILE METALS BY SUBLIMATION

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SEPARATING VOLATILE METALS BY SUBLIMATION

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This invention relates to the purification of metals by sublimation or evaporation, and has for its object broadly the separation of the volatile components of impure metals and alloys. In particular, I provide a method of effecting substantial or partial separation of the volatile components of alloys of the alkali and alkaline earth metals, especially magnesium.

In a copending application, Serial No. 598,292, which has matured into Patent 1,594,344 dated August 3, 1926, I have disclosed a commercial process of separating magnesium from relatively non-volatile impurities by sublimation. Magnesium commonly has volatile impurities present also, as for example sodium, which evaporate with it during sublimation and may contaminate the sublimed product. I have discovered, however, that by proper control of the conditions surrounding condensation of the metal vapor, separation of the volatile components of the mixture or alloy may also be effected.

In my process of sublimation the metal to be sublimed is heated in a retort to which is attached a condenser and accessory apparatus for producing a high vacuum in the system. In operation the pressure in the retort and condenser is reduced below the vapor pressure of the metal at the temperature to which it is to be heated for sublimation and heat is applied to the retort. The non-volatile substances remain in the retort and the volatile metal evaporates and is deposited on the walls of the condenser. In my above-mentioned application I have disclosed the fact that to obtain rapid sublimation, it is desirable to regulate or so adjust the operating pressure in the condenser that the vapor pressure of the solid metal in the retort is slightly greater than the total absolute pressure within the condenser. Under these conditions the evolution of metal vapor will be rapid, and if the proper condensation facilities are provided, the rate of sublimation is limited only by the rate of evaporation of the solid metal. The temperature at which the vapor pressure of the solid metal becomes greater than the absolute pressure of the system is hereinafter called the "sublimation point". By operating

at or above the sublimation point, I not only produce rapid sublimation but I also sweep out and away the residual amounts of air or other gases in the apparatus and thus decrease the possibility of these gases to combine with and thus introduce non-metallic impurities into the product.

In carrying out my present invention any suitable apparatus may be used, as for example one of the type described in my copending application above mentioned, to which reference may be made for a more complete description. The condenser is preferably of upright cylindrical form, equipped with a split lining of sheet metal which may be taken out for convenient removal of the metal deposited thereon. Such a lining, bearing the deposit of metal on its inner surface, is shown in the accompanying drawings, in which

Fig. 1 is a cross section on line 1—1 of Fig. 2, and Fig. 2 is a longitudinal section on line 2—2 of Fig. 1.

The sheet metal lining or liner 10 is split longitudinally as indicated at 11. The crystalline metal deposit is indicated at 12. The temperature conditions which must be maintained in the condenser are of prime importance. If only one volatile metal is present it is only necessary to maintain a condenser surface cold enough to cause the metal vapor to condense. When, however, two or more volatile metals are present a spatial separation can be effected, that is, the two metals can be caused to deposit on different zones of the condenser surface by maintaining these zones at different and successively lower temperatures, which are kept constant in any given run. One effective way of securing the proper temperature gradient on the condenser surface is to so proportion the length of the condenser, with respect to the temperature and heat input in the retort connected therewith, that the natural thermal conduction of heat from the retort to the condenser through its walls, in conjunction with the radiation or other cooling of the condenser, will maintain the desired conditions. External insulating, heating, and cooling devices of any convenient kind may also be employed for the purpose, enabling the tem-

perature to be regulated by manual control, or, if desired, automatically, as by thermostatic means.

As one specific illustration of my invention, I will describe the separation of magnesium from sodium by my "fractional" sublimation process. Sodium may commonly occur as an impurity in magnesium prepared by electrolytic reduction from an electrolyte containing sodium salts, and its removal is usually desirable. A suitable charge, say 100 pounds of crude magnesium containing about 0.5 per cent sodium, may be placed in the retort and heated under a pressure of about 0.5 to 0.2 mm. of mercury for a period of approximately 12 hours, maintaining a temperature of about 600° C. in the retort, and keeping the upper end of the condenser at about 90° C. The metal vapors crystallize on the split liner which is removable from the condenser and which may therefore be taken out and opened. The deposit usually has its greatest thickness a short distance from the bottom and from that point tapers off gradually, and it may extend the full length of the liner. At the extreme upper end the deposit may be only about one-sixteenth of an inch thick.

When the liner is first removed, the adhering crystalline deposit appears uniformly bright and silvery. An exposure to the air of about 10 to 20 minutes darkens a zone at the upper end, say down to about the point indicated by the arrow 13. Toward the lower edge of the zone the darkening becomes less noticeable and disappears at a sharply marked boundary, and I have observed the remarkable fact that this boundary is generally so sharply defined that a drop of phenolphthalein solution placed on the line turns distinctly red on the dark side and remains unchanged in color on the bright side of the deposit.

Analysis of the material above the line discloses as high as 85 per cent sodium in the deposit at the extreme upper end. This sodium content decreases as the boundary is approached, being from 1 to 2 per cent adjacent to the boundary, just above the region of bright crystals. An average analysis of the material below the line shows sodium to be present in amounts less than 0.05 per cent.

As the volatilized metal vapors impinge on the walls of the condenser the atoms of magnesium tend to condense because of the lower temperature in the condenser. At the lower (or warmer) end of the condenser, the temperature is relatively high compared with that at the other end. The more volatile sodium therefore does not condense on, or else evaporates readily from, the relatively hot lower surface and is carried on farther up the condenser to a cooler zone. When the temperature of the condensing surface is above the boiling point of sodium at the pressure in

the condenser, there is little tendency for the sodium to remain in and contaminate the magnesium crystals, but when the temperature of the condensing surface falls below this boiling point, the concentration of the sodium begins to build up rapidly.

Potassium is somewhat more volatile than sodium but its behavior is similar in the sublimation process and it is readily separable from magnesium by the present process.

Calcium may also be purified by my process, with separation of the volatile impurities such as sodium and potassium. In one example, which I may cite, a charge of 75 pounds of impure calcium was heated in the retort at temperatures which eventually rose almost to the melting point, which is about 810° C., and the metallic calcium was deposited in zones in the condenser with the more volatile impurities segregated at the upper end. The concentration of alkali metal at the upper end of the condenser was so high that parts of it ignited on opening the condenser and exposing the deposit to the air. The line of demarcation between the calcium and the more volatile impurities was indicated by a change in color on exposure to the atmosphere for a short time, much as in the case of the magnesium previously described. It is impossible to test with phenolphthalein, however, since the indicator turns pink when in contact with either the calcium or the alkali metal.

In some cases it may be impossible to effect a very sharp separation of the volatile metals because of their physical characteristics. I have found, for example, that if magnesium-zinc alloys are sublimed, both metals volatilize. The zinc is appreciably more volatile than the magnesium but is, nevertheless, usually found in appreciable but non-uniform quantities throughout the magnesium deposit. I have also found it impractical to effect a substantially complete separation of calcium and magnesium from each other. Even in these and other cases where complete or substantially complete separation cannot be accomplished a useful separation of the constituents may be obtained.

As previously stated, the temperature gradient in the condenser should be maintained substantially constant and may be regulated in any convenient manner, as for example by the simple expedient of one or more cooling coils around the condenser at appropriate points, through which the flow of water or other cooling fluid can be controlled in accordance with the interior temperatures as indicated by thermometers suitably located. Thermostatic regulation may be employed if automatic control is desired. In some cases it may be desirable to enclose more or less of the condensing column in a heat-insulating jacket or the like, including or excluding the cooling coil or coils, to con-

5 trol the escape of heat by convection and radiation and obtain a steeper gradient between adjoining temperature zones; though it is to be understood that anything like a sharp differentiation is unnecessary. The condenser should not be too short, or the results will not be satisfactory. In subliming magnesium or calcium at the rate of about 80 pounds in 8-10 hours or so, a cylindrical condenser about four feet long and fourteen inches in diameter inside has been found satisfactory.

10 The time of heating and the rate of evaporation are also factors in determining the extent of separation of the volatile metals. If the sublimation is too rapid there is greater tendency for the more volatile metals to be included in the deposit at the lower end of the condenser because the rate of condensation there is too rapid to admit of the ready re-evaporation of the small amounts (of the more volatile metal or metals) which are always condensing in that part of the condenser. The period of heating should therefore be sufficiently long to permit the desired separation to be effected in the particular condenser employed. This and other factors are best determined by experience with the particular mixture or alloy to be treated.

20 In carrying out the invention by evaporation of the metal in the liquid state, that is, by distillation, the pressure in the retort is maintained above the vapor pressure at the melting point of the metal in the retort, as by means of an inert gas or gases, for example argon, in the retort and condenser, or by throttling the retort outlet, and heat is supplied at a rate sufficient to produce melting, in whole or in part, of the contents of the retort. However, when operating by distillation a higher retort temperature is necessary, and the use of a foreign gas is usually inconvenient if not otherwise undesirable.

45 It is to be understood that the invention is not limited to the specific procedure herein described but can be carried out in other ways without departing from its spirit.

I claim—

50 1. Process of treating alkali and alkaline earth metals and alloys thereof, comprising evaporating the metals from a metallic mixture containing the same, and condensing the resulting metallic vapors directly to the solid state upon a condensing surface by passing the vapors over such surface while controlling the temperature of said surface so as to cause substantial spatial separation of the metals condensed thereon.

60 2. A process of subliming impure magnesium and magnesium alloys, in which condensible metallic vapors containing magnesium are produced, the step of condensing said vapors directly to the solid state in a condenser by controlling the temperature

conditions in the condenser so as to cause substantial concentration of the solid metals in different parts of the condenser.

3. In a process of subliming impure magnesium or magnesium alloy containing another volatile metal capable of condensing from vapor directly to the solid state, the step of maintaining on a condensing surface to receive the magnesium, zones of successively lower and substantially unvarying temperatures whereby different condensible metals, as they condense directly to the solid state, are concentrated in different zones of the condensing surface.

4. A process of separating alkali metal from impure magnesium or magnesium alloy, comprising subliming the volatile components under reduced pressure and condensing the magnesium directly to solid form on a surface the temperature of which is maintained above the point of volatilization of the alkali metal but below the sublimation point of magnesium and condensing the alkali metal directly to solid form on a surface of suitably lower temperature.

5. A process of subliming compositions containing alkali and alkaline earth metals under reduced pressure, comprising subliming the volatile components and condensing the metallic vapors directly to the solid state by passing vapors over a condensing surface while maintaining on the latter a temperature gradient ranging from below the sublimation point of the least volatile metal and above the sublimation point of the more volatile metal or metals to a suitably lower temperature.

6. A process of separating volatile metal constituents of a metallic mixture, comprising heating the mixture to volatilize the metals to be separated, and condensing the metallic vapors directly to the solid state by passing the vapors over a condensing surface of decreasing temperature while maintaining the temperature gradient substantially constant.

7. A process of separating volatile metal constituents of a metallic mixture, comprising heating the mixture to volatilize the metals to be separated, passing the metal vapors into the heated end of a tubular condenser, and regulating the escape of heat from the condenser to provide therein a substantially constant temperature gradient from the hotter to the cooler end and thereby causing the volatilized metals to condense directly to the solid form on the surface of the tubular condenser in the order of their boiling points and with substantial spatial separation.

In testimony whereof I hereto affix my signature.

HERMAN E. BAKKEN.