May 8, 1945. P. P. ALEXANDER 2,375,199

PURIFICATION OF METALS

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Fig. 1.

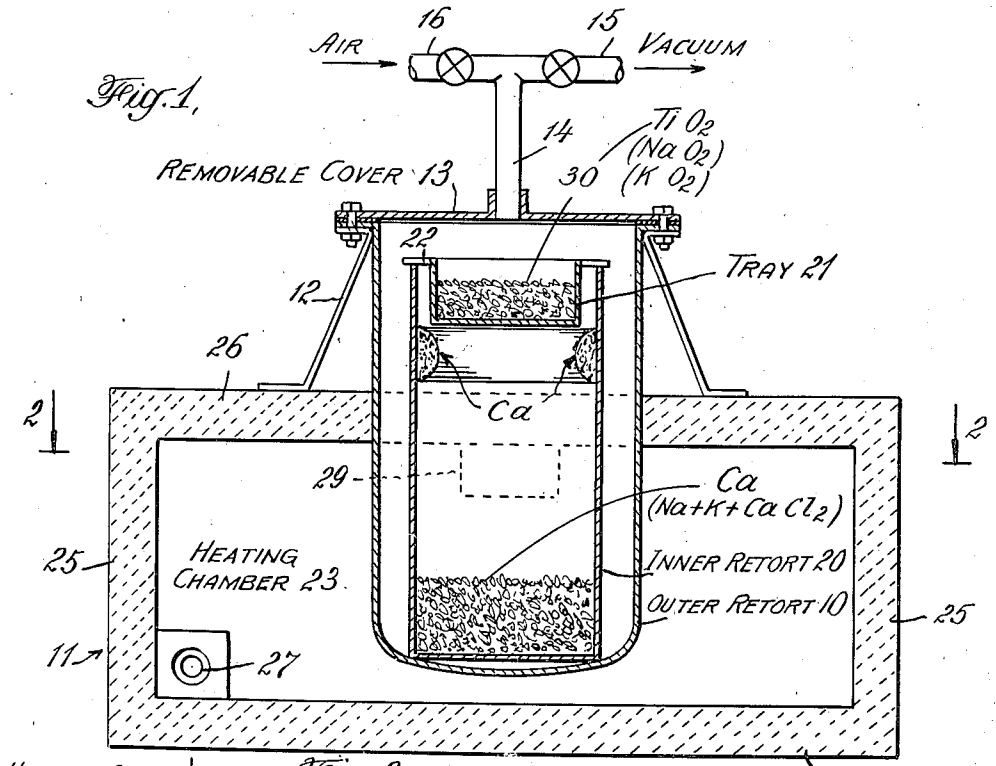
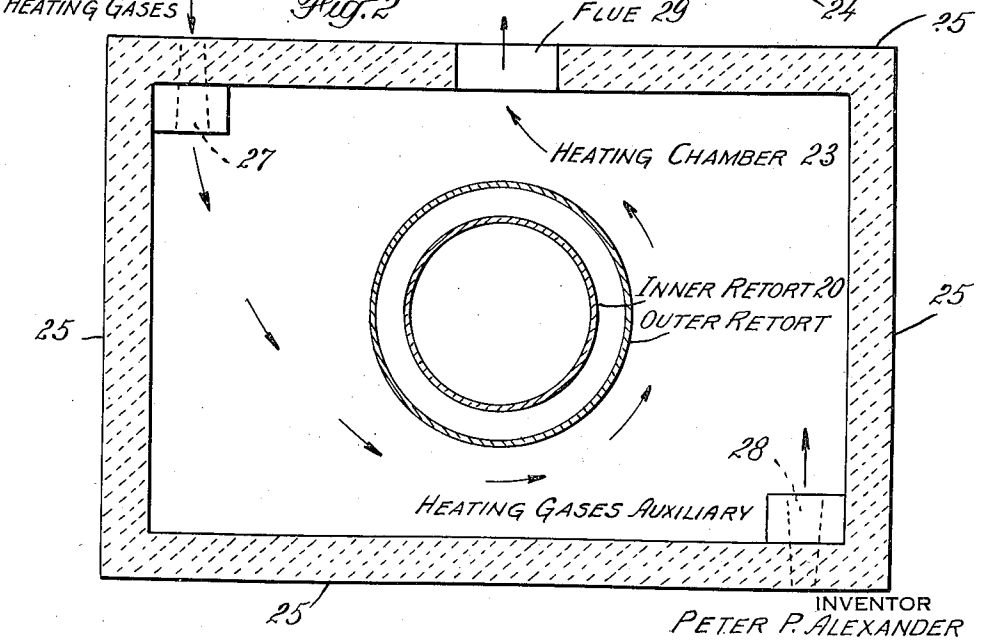


Fig. 2



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PURIFICATION OF METALS

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19 Claims. (Cl. 75—63)

This invention relates to the purification of metals contaminated with metal impurities having a lower boiling point, especially oxidizable metal impurities, and has for its object more particularly the purification of metals contaminated with one or more of the alkali metals.

The alkaline-earth metals, calcium, strontium and barium, are usually made by subjecting their fused chlorides to electrolysis. Since the salts of the alkali metals, sodium and potassium, are usually present in these chlorides, the resulting alkaline-earth metal is usually contaminated with a small amount of alkali metal, as well as of the chloride of the alkaline-earth metal itself. To purify the alkaline-earth metal, it has been proposed to subject the metal to distillation in a closed retort that has been evacuated to remove objectionable air. The distilled metal is permitted to condense in a cooler part of the retort, usually in the form of a more or less spongy deposit. After cooling the retort, air is admitted, the retort is opened and the condense metal is removed. The resulting product is so reactive that it frequently oxidizes rapidly on the surface and produces heat in sufficient amount to ignite the whole mass, with the result that fires are quite common. This objectionable result is all the more apt to occur because of the presence of the more highly reactive sodium and potassium. These alkali metals are also distilled and condense in a cooler part of the retort. The small deposits of sodium and potassium are so reactive that they almost invariably catch fire when the retort is opened and they come in contact with the oxygen of air.

Magnesium is produced pyrometallurgically and electrolytically. It is common in both methods to encounter the alkali metals, particularly sodium and potassium because they are found with the magnesium in nature. With sea water or magnesium-bearing ores as the source of the magnesium, there is a marked tendency for sodium and potassium to be present in electrolytic magnesium in amounts that are objectionable for some purposes. When magnesium-bearing ores are subjected to reduction pyrometallurgically, for example, in a retort that has been evacuated to remove objectionable air, and the reduced magnesium is distilled and condensed, sodium and potassium tend to follow the magnesium and are usually condensed in a cooler zone. Fires are not uncommon when the retort, or its associated condenser, is opened and the sodium and potassium first contact the oxygen of the air. Special precautions are taken to condense magnesium separate from the sodium and potassium and to remove the sodium and potassium without starting a fire. A special condenser for the sodium and potassium is usually provided at the coolest end of the retort, removed from the zone in which the magnesium is condensed; but the condensed sodium and potassium may nevertheless catch fire on exposure to the air.

As a result of my investigations I have discovered that these disadvantages may be overcome for the most part. The alkali metals, sodium and potassium, may be segregated from the higher boiling point metal to be purified and converted into compounds that are non-inflammable on exposure to the oxidizing influence of air. The metal to be purified may be separately collected and in some instances be freed of other impurities.

In accordance with the invention, the metal to be purified is heated in the absence of air to a temperature sufficiently high to distill the alkali metal impurity. The resulting alkali metal vapor impurity is then selectively oxidized. This may be accomplished by bringing the alkali metal vapor impurity into reactive contact with a refractory metal oxide, such as titanium oxide, zirconium oxide and chromium oxide, and collecting the oxidized alkali metal impurity as a solid separate from the metal to be purified. The metal to be purified is itself advantageously distilled in some cases and condensed separate from the oxidized alkali metal impurity.

These and other features of the invention may be better understood by referring to the accompanying drawing, taken in conjunction with the following description, in which:

Fig. 1 is a diagrammatic representation, being a side elevation in section, of an apparatus with which the method of the invention may be practiced; and

Fig. 2 is a horizontal section on the line 2—2 of Fig. 1.

The apparatus shown comprises an outer retort 10 supported within a heating furnace 11, the retort being held in position by means of two or more supports 12 resting on top of the heating furnace. The retort preferably consists of heat-resistant steel. It is provided with a removable cover 13 having attached thereto a vertical pipe 14 and lateral valved branches 15 and 16, connectable with a source of vacuum, and air, respectively. A removable inner retort 20, having an open top, rests within the outer retort. A removable tray 21 rests over the open top of the retort, being supported thereon by means of three or more lugs 22 extending over the wall of the inner retort. The heating furnace 11 consists essentially of a rectangular chamber 23 having a refractory bottom 24, side and end walls 25, and a top 26 having an opening of a size adapted to receive the outer retort. An expanding opening 27 is provided at or near a lower corner of one of the side walls of the chamber, for the introduction of heating gases into the chamber. A similar opening 28 is preferably provided at or near an opposite corner, as a spare or auxiliary means for

introducing heating, or cooling, gases into the chamber. When not in use, the opening 28 is closed. A flue opening 29 extends through the same wall as the opening 27, preferably at a higher level, so that heating gases passed into the chamber through the opening 27 tend to pass around the retort before leaving the chamber through the flue opening 29.

The apparatus may be used as follows: A charge of calcium, for example, contaminated with sodium, potassium, and calcium chloride, is placed in the bottom of the inner retort 20. The inner retort is then placed in the outer retort 10. A layer of titanium oxide 30 is placed in the tray 21, which is in turn placed across the open top of the inner retort. The removable cover 13 is placed on the outer retort 10 and locked thereon to provide a sealed joint. The lateral branch 15 is then connected to a source of vacuum. With the valve of this lateral branch open, and the valve of the other lateral branch 16 closed, the outer and inner retorts are placed under vacuum to remove objectionable air.

Heating gases are passed through opening 27 into the heating chamber, where they circulate almost completely around the retort and then pass through the flue opening 29 to the outside atmosphere. As the lower portion of the outer retort 10 is heated, the lower portion of the inner retort 20 is also heated. As the temperature rises, a point is reached where the sodium and potassium present in the calcium are distilled. The resulting sodium and potassium vapors rise to the upper and cooler portion of the retort where they come in contact with the titanium oxide 30 in the tray 21. Due to their great affinity for oxygen, the sodium and potassium are promptly oxidized and the titanium dioxide is reduced to titanium and a sub-oxide of titanium, according to reactions which may be indicated as follows:

$$Na+TiO_2 \rightarrow NaO_2+Ti$$

$$Na+4TiO_2 \rightarrow NaO_2+2Ti_2O_3$$

$$K+TiO_2 \rightarrow KO_2+Ti$$

$$K+4TiO_2 \rightarrow KO_2+2Ti_2O_3$$

As the temperature at the bottom of the inner retort continues to rise, a point is reached where the calcium is distilled and its resulting vapor tends to condense and settle out against the wall of the inner retort immediately below the tray 16. Some calcium vapor may of course rise sufficiently to come in contact with titanium dioxide in the tray and react with it in a manner similar to sodium or potassium vapor. The bulk of the distilled calcium may, however, be separately condensed and collected, as shown. A residue consisting essentially of calcium chloride, admixed perhaps with a small amount of sodium chloride or potassium chloride, or both, remains as a residue in the bottom of the inner retort.

The introduction of heating gases to the heating chamber is stopped and the retort is permitted to cool. The cooling operation may be accelerated by passing cooling air through the heating chamber, for example, through the opening 28, or by removing the outer retort and its contents from the heating chamber. After the retort has been suitably cooled, lateral branch 16 is opened to admit air to the interior of the retorts, after which the cover 13 is removed. The inner retort and tray are pulled out of the outer retort; the tray is removed, and the condensed calcium is scraped off and separately recovered. The residues are advantageously removed by washing the inner retort with water.

It will be clear to those skilled in this art that the invention lends itself to numerous modifications. Other metals of higher boiling point, such as barium, strontium, magnesium, etc., may be similarly treated to remove metal impurities of lower boiling point, such as the alkali metals, sodium and potassium, to convert them into harmless compounds. Instead of titanium oxide other suitable refractory metallic oxide, such as zirconium oxide and chromium oxide, may be employed, either separately or admixed. While the specific example relates to the purifying of a primary metal, it will be clear that the invention also lends itself to a smelting operation in which the metal to be purified is reduced from its compounds and the alkali metal impurity is selectively oxidized. This modification may be employed, for example, in conjunction with the above mentioned method of producing magnesium pyrometallurgically. According to a well-known practice, magnesium oxide is reduced with silicon or ferro-silicon and distilled in an externally heated retort placed under vacuum to remove objectionable air. The distilled magnesium is condensed in a cooler part of the retort or in a condenser specially provided for the purpose. The alkali metal impurities, sodium and potassium, are likewise reduced and distilled. In accordance with the present invention, they are converted into harmless compounds by selectively oxidizing them in the manner described.

In the practice of the invention, advantage is taken of the relative boiling points of the metals. The boiling points of the alkali metals, sodium and potassium, are substantially below those of the metals to be purified. The temperature of the metal to be purified is, therefore, gradually elevated to a point where the metal impurity of lower boiling point is distilled. By heating its bottom, the retort is caused to yield a graduated temperature range. Since the alkali metals have the lower boiling points, their vapors tend selectively to rise highest in the retort. Since the metals to be purified have the higher boiling points, their vapors do not tend to rise as high in the retort. They soon meet a temperature environment conducive to condensation. In other words, the metals to be purified may be made to condense in an intermediate section of the retort where the temperature is high enough to keep the alkali metal impurities in vapor form. The alkali metal vapors, on the other hand, tend to rise to a cooler portion of the retort, where they were heretofore condensed, but where they are now converted into harmless compounds in accordance with the invention.

This application is a continuation-in-part of my co-pending application Serial No. 478,095, filed March 5, 1943.

I claim:

1. In the method of purifying metals of higher boiling point contaminated with an alkali metal impurity of lower boiling point, the improvement which comprises heating the metal to be purified in the absence of air to a temperature sufficiently high to distill the alkali metal impurity but not the metal to be purified, selectively oxidizing the resulting alkali metal impurity vapor in a zone removed from the main body of metal to be purified, and collecting the oxidized alkali metal impurity as a solid separate from the metal to be purified.

2. Method according to claim 1, in which the

resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with a refractory metal oxide in a zone removed from the main body of metal to be purified.

3. Method according to claim 1, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with titanium oxide in a zone removed from the main body of metal to be purified.

4. Method according to claim 1, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with zirconium oxide in a zone removed from the main body of metal to be purified.

5. Method according to claim 1, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with chromium oxide in a zone removed from the main body of metal to be purified.

6. Method according to claim 1, in which the metal to be purified is also distilled, and condensing the resulting vapor of the metal to be purified as a solid separate from the oxidized alkali metal impurity in a zone intermediate that in which the alkali metal impurity is oxidized and that from which the main body of metal to be purified is distilled.

7. In the method of purifying metals of higher boiling point contaminated with an alkali metal impurity of lower boiling point, the improvement which comprises heating the metal to be purified in the absence of air to a temperature sufficiently high to distill the alkali metal impurity but not the metal to be purified, said alkali metal impurity being at least one of the group: sodium and potassium, selectively oxidizing the resulting alkali metal impurity vapor in a zone removed from the main body of metal to be purified, and collecting the oxidized alkali metal impurity as a solid separate from the metal to be purified.

8. Method according to claim 7, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with a refractory metal oxide in a zone removed from the main body of metal to be purified.

9. Method according to claim 7, in which the metal to be purified is also distilled, and condensing the resulting vapor of the metal to be purified as a solid separate from the oxidized alkali metal impurity in a zone intermediate that in which the alkali metal impurity is oxidized and that from which the main body of metal to be purified is distilled.

10. In the method of purifying magnesium contaminated with an alkali metal impurity, the improvement which comprises heating the magnesium in the absence of air to a temperature sufficiently high to distill the alkali metal impurity but not the magnesium, selectively oxidizing the resulting alkali metal impurity vapor in a zone removed from the main body of magnesium to be purified, and collecting the oxidized alkali metal impurity as a solid separate from the main body of magnesium to be purified.

11. Method according to claim 10, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with a refractory metal oxide in a zone removed from the main body of magnesium to be purified.

12. Method according to claim 10, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with titanium oxide in a zone removed from the main body of magnesium to be purified.

13. Method according to claim 10, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with zirconium oxide in a zone removed from the main body of magnesium to be purified.

14. Method according to claim 10, in which the resulting vapor of the alkali metal impurity is selectively oxidized by bringing it into reactive contact with chromium oxide in a zone removed from the main body of magnesium to be purified.

15. Method according to claim 10, in which the magnesium to be purified is also distilled, and condensing the resulting magnesium vapor as a solid separate from the oxidized alkali metal impurity in a zone intermediate that in which the alkali metal impurity is oxidized and that from which the main body of magnesium is distilled.

16. In the method of purifying magnesium contaminated with an alkali metal impurity, the improvement which comprises heating the magnesium in the absence of air to a temperature sufficiently high to distill the alkali metal impurity but not the magnesium, said alkali metal impurity being at least one of the group: sodium and potassium, selectively oxidizing the resulting alkali metal vapor impurity in a zone removed from the main body of magnesium to be purified, and collecting the oxidized alkali metal impurity as a solid separate from the magnesium.

17. In the method of purifying magnesium contaminated with an alkali metal impurity, the improvement which comprises heating the magnesium in the absence of air to a temperature sufficiently high to distill the alkali metal impurity but not the magnesium, selectively oxidizing the resulting alkali metal impurity vapor by bringing it into reactive contact with a refractory metal oxide in a zone removed from the main body of magnesium to be purified, collecting the oxidized alkali metal impurity as a solid separate from the main body of magnesium to be purified, distilling the magnesium, and condensing the resulting magnesium vapor as a solid separate from the oxidized metal impurity in a zone intermediate that in which the alkali metal impurity is oxidized and that from which the main body of magnesium is distilled.

18. In the method of purifying metals of relatively low boiling points contaminated with readily oxidizable metal impurities of lower boiling points, the improvement which comprises heating the metal to be purified in the absence of air to a temperature sufficiently high to distill the metal impurity but not the metal to be purified, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible refractory metal oxide in a zone removed from the main body of metal to be purified, and collecting the oxidized metal impurity as a solid separate from the metal to be purified.

19. Method according to the preceding claim, in which the metal to be purified is also distilled, and condensing the resulting vapor of the metal to be purified as a solid separate from the oxidized metal impurity in a zone intermediate that in which the metal impurity is oxidized and that from which the main body of metal to be purified is distilled.

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