

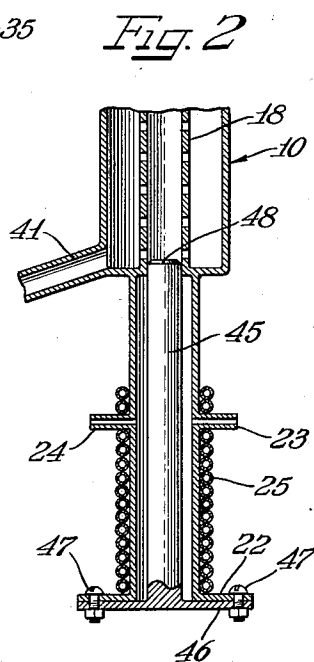
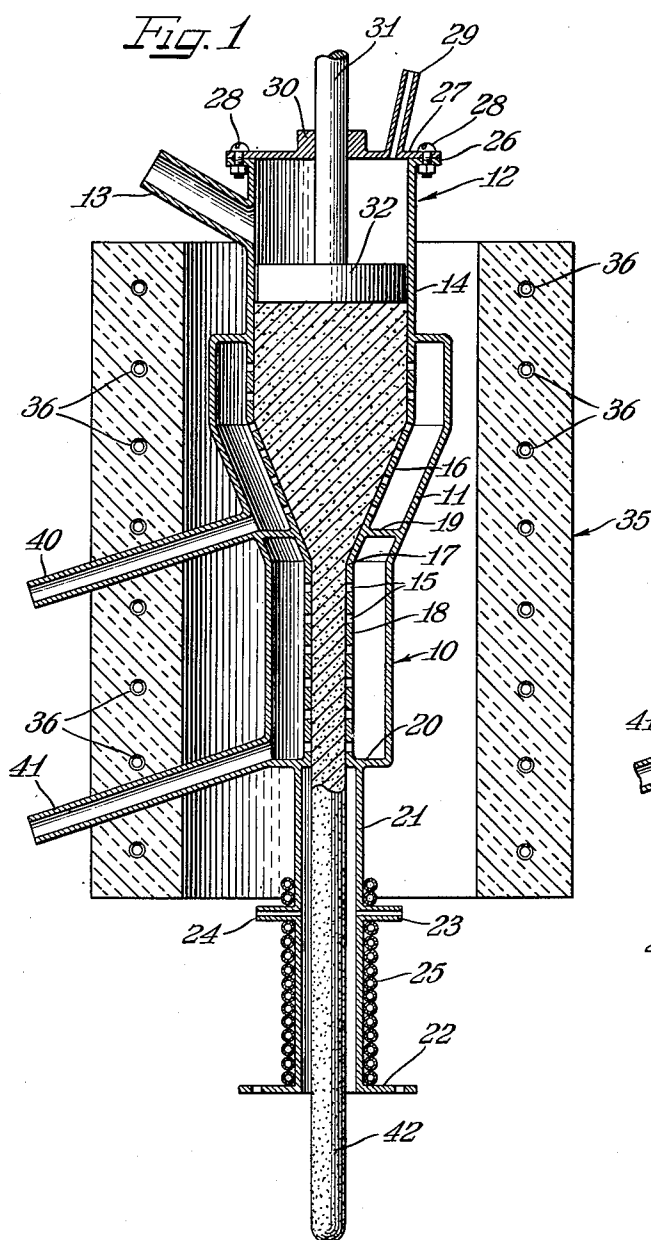
April 27, 1954

G. G. HATCH

2,676,882

METHOD FOR RECOVERING REFRACTORY METALS

Filed May 31, 1950



Inventor
Gerald G. Hatch

by *The Firm of Charles Mills* Attys

UNITED STATES PATENT OFFICE

2,676,882

METHOD FOR RECOVERING REFRACTORY METALS

Gerald G. Hatch, Chicago, Ill., assignor, by mesne assignments, to Kennecott Copper Corporation, New York, N. Y.

Application May 31, 1950, Serial No. 165,346

4 Claims. (Cl. 75-201)

1

The present invention relates to a method for recovering elemental metal from admixture with compounds having lower fusing temperatures than the metal.

The present invention is particularly adapted to a method for the recovery of elemental titanium from a reaction mixture produced in accordance with the method disclosed in Glasser and Hampel application Serial No. 90,954, now Patent No. 2,618,549, granted November 18, 1952, entitled "Method for the Production of Titanium," and assigned to the same assignee as the present application. It will be realized, however, that the features of the invention may be utilized in connection with the recovery of refractory metals other than titanium, such as, for example, zirconium, beryllium, chromium, cobalt, manganese, molybdenum, nickel, platinum, silicon, tungsten, and the like, and that it will also be applicable to the recovery of refractory metals from admixture with salts of reducing metals such as sodium, potassium, lithium, calcium, strontium, barium, and magnesium.

Briefly, the above-described process consists in reacting liquid titanium tetrachloride with an alkali metal amalgam such as sodium amalgam to form a reaction product containing powdery titanium particles, sodium chloride, together with any sub-halides of titanium produced in the reaction, as well as residual mercury. Since the sodium content of the original amalgam is generally quite low and since an excess of sodium in the amalgam with respect to titanium tetrachloride is used, large quantities of mercury appear in the reaction product. The removal of such large quantities of mercury is a considerable task, since the mercury adheres readily to the reaction product. While the mercury can be removed by distillation or gravity filtration, these are very time-consuming and expensive operations.

With the foregoing in mind, an object of the present invention is to provide a convenient method for the recovery of refractory metal from admixture with compounds having lower fusing points than the metal.

A further object of the present invention is to provide a method for the removal of mercury and substantial amounts of sodium chloride from a reaction product of an amalgam reduction process.

Still another object of the present invention is to provide a method for recovering the titanium in such a reaction product in a coherent form mixed with sodium chloride, from which metallic titanium can be more readily recovered.

2

Yet another object of the present invention is to provide a compressed mixture of titanium metal and sodium chloride crystals from which titanium metal can be readily recovered, and which is stable in air, water, and other reagents.

A further object of the present invention is to provide an apparatus for removing mercury and sodium chloride from reaction mixtures of the type described.

Other objects and features of the present invention will be apparent from the following description and the appended claims.

The method of the present invention generally consists of compressing the reaction product from the amalgam reaction, which will contain powdery titanium, mercury, and sodium chloride under elevated temperatures to thereby squeeze out all or a major portion of the mercury present and also substantial quantities of the sodium chloride. This compression is effected in the presence of an inert gas such as argon, helium, neon, krypton, and the like, under substantially atmospheric pressures. The reaction mixture is compressed to a coherent shape preferably containing at least 35% by weight titanium with the balance being essentially sodium chloride. This mixture can then be treated for the recovery of metallic titanium in any one of a number of manners. For example, the mixture may be introduced into an arc melting furnace as a consumable electrode according to the method described in my copending application Serial No. 165,347, now abandoned, filed concurrently herewith. Another method for the recovery of titanium from such a mixture which may be used is the vacuum distillation of the sodium chloride present. In addition, the rod can be conveniently melted in an induction furnace where the sodium chloride is removed by volatilization.

The advantages of the present invention are quite substantial. For one, the compression of the titanium into coherent form directly upon removal from the reaction zone removes the tendency for the titanium to become contaminated, since the crystals of titanium are compressed into a much less reactive form than the sub-microscopic particles which are produced by the reaction. Further, vacuum conditions are not essential in the removal of mercury and sodium chloride according to the present invention, but such removal may be effected in the presence of an inert gas at substantially atmospheric pressures. The process also has the advantage of flexibility in that it can be made part of a continuous or semi-continuous process by using the

process of the present invention in conjunction with an amalgam reduction process and feeding the final compressed product into an arc melting furnace as a consumable electrode.

Another advantage arising from the present invention is the fact that mercury and sodium chloride can be removed in one step if such is desired. Previously, resort has been made to the use of gravity type filters or distillation to remove most of the mercury prior to the treatment of the reaction mass for the removal of sodium chloride. By removing the sodium chloride in accordance with the present invention, a considerable amount of heat is saved, since the heat required is only sufficient to melt the sodium chloride and not necessarily to vaporize it.

Another advantage which can be realized by the practice of the present invention is the convenience by which titanium alloys can be prepared. Thus, the alloying elements may be added to the reaction mass prior to the compression step before the removal of mercury and sodium chloride, and the alloying elements are carried through the compression step into the final compressed mixture.

A very important advantage arising from the present invention is that the titanium rod or pencil which is produced as a result of the compression contains agglomerated particles of titanium which are sufficiently large to be stable upon exposure to air. Thus, the compressed product may be stored for indefinite periods prior to further treatment.

While the foregoing description of the process was concerned with the recovery of elemental titanium by a reaction involving reduction with a sodium amalgam, it will be appreciated that the same process can be applied to the recovery of other reactive metals, such as zirconium, which, in finely divided form, are extremely reactive to air, oxygen, nitrogen and aqueous liquids. As mentioned previously, the process is also applicable to the recovery of titanium and other refractory metals from admixture with salts of reducing metals such as the alkali metals, alkaline earth metals, and magnesium.

The apparatus used to carry out the process of the present invention may assume a variety of forms. One such apparatus may be a suitably heated screw type extrusion machine. Another type is illustrated in the attached sheet of drawings, in which:

Figure 1 is a cross-sectional view of an apparatus designed to carry out the process of the present invention; and

Figure 2 is a fragmentary cross-sectional view of the lower portion of the apparatus showing the condition at the beginning of the compression operation.

As shown on the drawing:

Reference numeral 10 denotes generally a casing consisting of an outer jacket 11 and an inner casing 12. The inner casing 12 has an inlet 13 formed therein for receiving the products from the reaction zone which will normally comprise a large percentage of mercury, sodium chloride, and titanium metal in the form of a very fine powder. Below the inlet 13, there is a cylindrical reservoir portion 14 having a relatively large number of perforations 15 therearound. For the sake of better illustration, the size of the perforations 15 has been exaggerated in the drawings, as the actual size of such perforations will normally be less than about $\frac{1}{8}$ of an inch in diameter.

The inner casing 12 below the reservoir portion 14 is formed with a tapered perforated wall portion 16. The tapered wall portion 16 terminates in a restricted orifice 17 having a perforated conduit 18 depending therefrom. A baffle 19 is disposed between the tapered wall portion 16 and the outer jacket 11, and a second baffle 20 between the conduit 18 and the jacket 11 is provided for purposes which will be hereinafter described.

At the base of the outer jacket 11 and the perforated conduit 18, is a cylindrical member 21 having a base flange 22 which can be secured to the inlet of an arc melting furnace where the compressed product is to be used as a consumable electrode in an arc melting process. An inlet 23 and an outlet 24 are provided along the cylinder 21 for circulating an inert gas such as argon and the like within the cylinder 21. A cooling coil 25 around the base of the cylinder 21 is provided to aid in freezing the compressed mixture after the removal of some of its sodium chloride content.

The top of the casing 12 is provided with a peripheral flange portion 26 to which is secured a closure member 27, as by means of bolts 28. The closure member 27 is provided with an inlet 29 for introducing an inert gas of the type described within the casing 12. A boss 30 on the closure member 27 has an axial bore there-through for slidably receiving a shaft 31 carrying a plunger 32. The diameter of the plunger 32 is only slightly smaller than the interior diameter of the casing 12 so that the plunger 32 is freely reciprocable within the reservoir portion 14 of the assembly, and permits the inert gas from the inlet 29 to flow past the plunger 32.

The casing 10 and its adjuncts are disposed within a furnace 35 having a plurality of spaced heating elements 36 therein which control the temperature of the furnace. Provision should be made for independently controlling the temperatures attained by the various heating elements since it is desirable to operate the upper section of the furnace at a substantially lower temperature than the bottom of the furnace.

The operation of the apparatus shown in Figure 1 will now be described. The furnace temperatures are adjusted so that the temperature at the tapered wall portion 16 of the casing is below the melting point of sodium chloride, and normally within the range from room temperature to 1500° F. and preferably from 600° to 1500° F. The lower portion of the furnace is operated at a somewhat higher temperature, so that the temperature below the restricted orifice 17 is above the melting point of sodium chloride, and, where the system is operated under an atmospheric pressure of argon, this temperature will be in the range from about 1500° to 1800° F. However, these ranges of temperatures may overlap, as long as a sufficiently long section of the apparatus is operated at a temperature above the melting point of the salt to be removed.

A supply of reaction products from the amalgam reaction zone is introduced into the casing through the inlet 13 and is compressed by downward strokes of the plunger 32 against the tapered side wall 16 and through the orifice 17 of the inner casing 14. The tapered side wall 16 effectively magnifies the compressive force exerted by the plunger 32 so that most of the mercury is removed before the reaction mixture passes through the orifice 17. The mercury is removed by gravity flow through a downwardly inclined discharge pipe 40 formed in the outer

jacket 11 and extending through the furnace 35.

The mixture entering the restricted orifice 17 is free or substantially free from mercury, and consists essentially of titanium crystals and sodium chloride. Since the temperature occurring below the orifice 17 is above the melting point of sodium chloride, further compression of the mixture at these temperatures causes the sodium chloride to flow through the perforations in the conduit 18 and accumulate on the baffle 20, from which it may be drained through a discharge conduit 41 in communication therewith. Sodium chloride is remarkably fluid at temperatures even slightly above its melting point, so that a large amount of the sodium chloride present can be removed through the compression operation. It will be understood that the process can be carried out to remove practically all of the sodium chloride, but this is not usually the most economical mode of procedure.

In normal instances, enough sodium chloride will be removed during the compression to form a mixture of titanium and sodium chloride having at least 35% by weight titanium. A suitable rod for use as a consumable electrode in an arc melting process is prepared by carrying out the compression of the mixture until a compact containing about 75% titanium and 25% sodium chloride remains.

The compressed product, as illustrated in Figure 1, is in the form of a self-sustaining rod 42. The compression of the titanium crystals at the elevated temperatures used for removing sodium chloride is sufficient to agglomerate very fine particles of titanium metal originally present into a stable form so that the finished rod 42 is stable in air and may be stored for extended periods prior to recovery of metallic titanium therefrom. To facilitate the freezing of the extruded mixture of titanium and sodium chloride crystals after the removal of substantial portions of the sodium chloride, the cooling coils 25 are provided with a circulating cooling medium such as water.

The apparatus shown in Figure 1 is shown in the course of a continuous extrusion operation where the rod 42 is continuously fed through the flange 22 of the cylinder 21. To initiate the original compression, an anvil 45 (Fig. 2) having a base portion 46 secured to the flange 22 by means of bolts 47 is inserted within the cylinder 21. The anvil 45 has a tapered upper end portion 48 arranged to be snugly seated within the bore of the cylinder 21. The anvil 45 is maintained in this position until a sufficient amount of the reaction product has been introduced into the system and the plunger 32 has compressed the mass until the compressed mixture at the base of the conduit 18 is sufficiently rigid to form a self-sustaining structure. Thereupon, the anvil 45 is removed and the extrusion may be operated continuously as illustrated in Figure 1.

The reduction in volume of the reaction product within the apparatus is quite substantial, being on the order of 20 times or more.

While the present invention has been described primarily with respect to treating a reaction product containing large amounts of mercury, it is evident that the same system is applicable to the treatment of a substantially mercury-free reaction product consisting essentially of titanium powder and sodium chloride for the removal of sodium chloride.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. In a method of recovering elemental titanium from a reaction mass containing finely divided titanium metal, mercury and sodium chloride, the steps comprising: first, compressing said mass against a conical perforate barrier converging in the direction of the compressive force, maintaining the temperature of said mass below the melting point of sodium chloride, expressing substantially all of the mercury through said conical perforate barrier to leave a comparatively mercury-free mass; next compressing said latter mass into the bore of a cylindrical perforate barrier formed as a continuation of said conical barrier, maintaining said latter mass at a temperature above the melting point of sodium chloride, expressing a substantial amount of sodium chloride through said cylindrical perforate barrier; and, finally, extruding the remaining mass from said cylindrical perforate barrier as a coherent rod containing at least 35% elemental titanium by weight thereof.

2. In a method of recovering elemental titanium from a reaction mass containing finely divided titanium metal, mercury and sodium chloride, the steps comprising: first, compressing said mass against a conical perforate barrier converging in the direction of the compressive force, maintaining the temperature of said mass at from 600° to 1500° F., expressing substantially all of the mercury through said conical perforate barrier to leave a comparatively mercury-free mass; next compressing said latter mass into the bore of a cylindrical perforate barrier formed as a continuation of said conical barrier, maintaining said latter mass at a temperature of from 1500° to 1800° F. to liquefy the sodium chloride, expressing a substantial amount of sodium chloride through said cylindrical perforate barrier; and, finally, extruding the remaining mass from said cylindrical perforate barrier as a coherent rod containing at least 35% elemental titanium by weight thereof.

3. In a method of recovering a refractory metal from a reaction mass containing said refractory metal in finely divided form, mercury and a chloride of a metal selected from the group consisting of alkali metals, alkaline earth metals and magnesium, the steps comprising: first, compressing said mass against a conical perforate area converging in the direction of the compressive force, maintaining the temperature of said mass below the melting point of the chloride of the metal selected, expressing substantially all of the mercury through said conical perforate barrier to leave a relatively mercury-free mass; next, compressing said latter mass into the bore of a cylindrical perforate barrier formed as a continuation of said conical barrier, maintaining said latter mass at a temperature above the melting point of the chloride of said selected metal, expressing a substantial amount of said chloride through said cylindrical perforate barrier; and, finally, extruding the remaining mass from said cylindrical perforate barrier as a coherent rod containing at least 35% of the refractory metal by weight thereof.

4. In a method of recovering elemental titanium from a reaction mass containing finely di-

7

vided titanium metal, mercury and sodium chloride, the steps comprising: first, compressing said mass against a conical perforate barrier converging in the direction of the compressive force, maintaining the temperature of said mass below the melting point of sodium chloride, expressing substantially all of the mercury through said conical perforate barrier to leave a comparatively mercury-free mass; next, compressing said latter mass into the bore of a cylindrical perforate barrier formed as a continuation of said conical barrier, maintaining said latter mass at a temperature above the melting point of sodium chloride, expressing a sufficient amount of sodium chloride through said cylindrical perforate barrier to impart to the remaining mass a composition consisting essentially of about 75% of titanium metal and about 25% of sodium chloride by weight of said mass; and, finally, extruding said remaining mass from said cylindrical perforate barrier as a coherent, self-sustaining rod.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,648,678	Ehlers	Nov. 8, 1927

25

8

Number	Name	Date
2,171,439	Von Zeppelin	Aug. 29, 1939
2,205,854	Kroll	June 25, 1940
2,205,865	Schwarzkopf	June 25, 1940
2,207,461	Kemp	July 9, 1940
2,470,269	Shaefer	May 17, 1949
2,471,899	Regner	May 31, 1949
2,479,641	Ripich	Aug. 23, 1949
2,482,127	Schlechten et al.	Sept. 20, 1949
2,607,674	Winter, Jr.	Aug. 19, 1952

FOREIGN PATENTS

Number	Country	Date
296,867	Germany	Mar. 13, 1917

OTHER REFERENCES

The Metal Industry, July 12, 1940, pages 27-30, inclusive. Article by Jones.

U. S. Air Force Project Rand, Titanium and Titanium-Base Alloys. Published March 15, 1949, by The Rand Corp., Santa Monica, Calif. Page 52.

20