

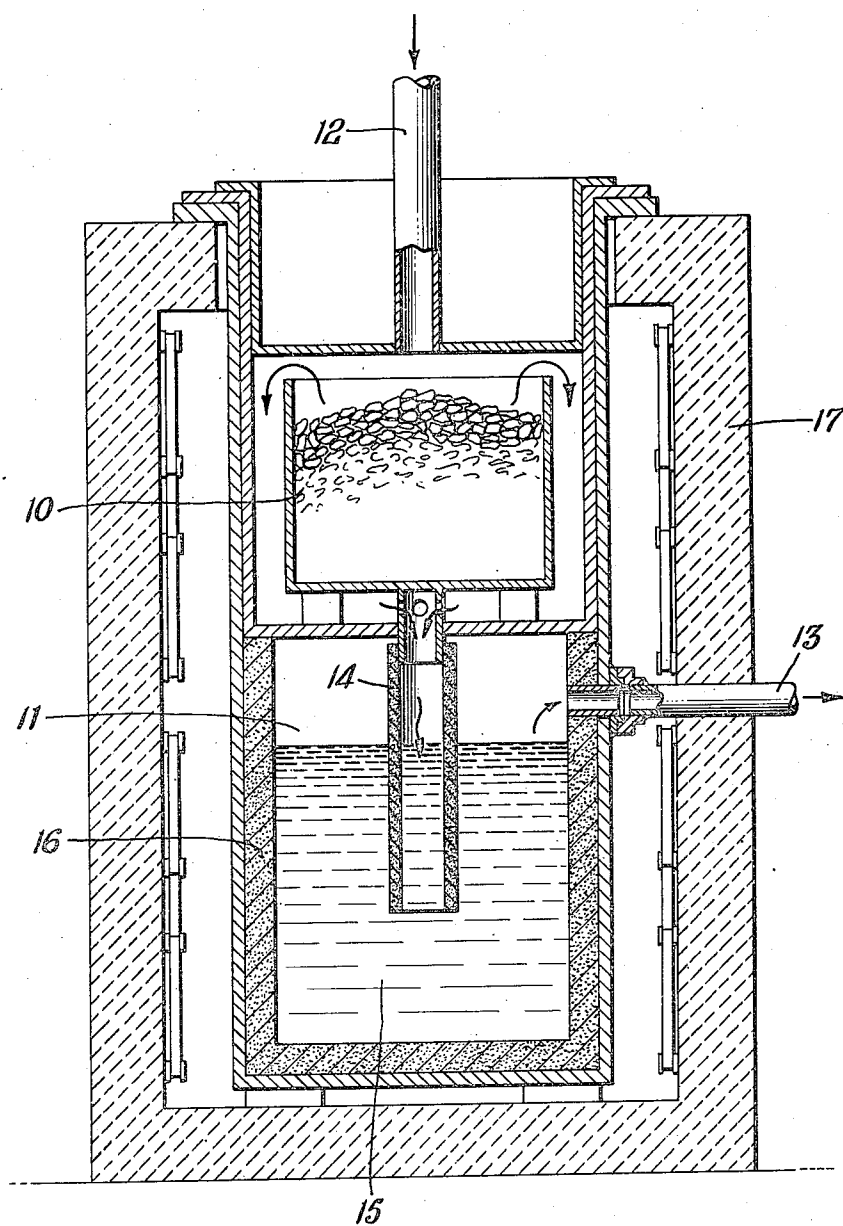
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PROCESS FOR PRODUCING ZIRCONIUM CHLORIDE

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PROCESS FOR PRODUCING ZIRCONIUM CHLORIDE

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This invention relates to the preparation of zirconium, and more specifically refers to a novel process for preparing from zirconium-silicon alloys, zirconium chloride and, therefrom, zirconium of commercial quality. This application is in part a continuation of our application Ser. No. 502,041, filed September 11, 1943, now abandoned.

The principal use for zirconium in the metallic state is in the manufacture of steel. For that use ferrozirconium, which ordinarily contains silicon, and the zirconium-silicon-iron alloy usually termed silicon-zirconium, are quite satisfactory and are widely available in several commercial grades.

A purer form of metallic zirconium is demanded for some other uses, for instance in the manufacture of nonferrous alloys. The demand has generally been met commercially by reducing zirconium compounds with calcium or sodium or by a vapor phase decomposition of zirconium halides. Although these methods yield zirconium of good quality, they require relatively expensive iron-free zirconium salt as the raw material.

An object of this invention is to produce zirconium of high quality by an economical process which may use relatively inexpensive and readily available raw materials. A further object is a novel method for producing substantially iron-free zirconium chloride suitable for use to produce a good grade of zirconium. Another object is to provide a novel process for producing zirconium of high quality from zirconium-silicon-iron alloys of ordinary commercial purity, such as silicon-zirconium and ferrozirconium.

In its most general aspect the method of the invention comprises contacting a zirconium-silicon alloy with an anhydrous metal halide which has a materially smaller heat of formation than the corresponding zirconium halide, preferably with iron chloride, at an elevated temperature below the melting point of the alloy, to form zirconium halide.

The alloy should be in a finely-divided state, preferably fine enough to pass a 100 mesh screen. The zirconium content of the alloy is not critical, and may be as low as 10% and up to 50% or more.

One manner of practicing the method of this invention comprises intimately mixing, in the solid state, zirconium-silicon-iron alloy and ferrous chloride; heating the mixture to a reaction temperature above about 220° C. and below the melting point of the ferrous chloride, thereby generating vapors of zirconium chloride and silicon chloride; and separating and recovering the

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zirconium chloride which may then be reduced to zirconium. Preferably, the separation and recovery is effected by passing the chloride vapors through a mass of salt which selectively removes the zirconium chloride; but as an alternative the zirconium chloride may be condensed at a temperature at which silicon chloride is still in the vapor phase.

To obtain an intimate mixture, the zirconium-silicon-iron alloy and ferrous chloride should be comminuted and intermingled, and are preferably briquetted. Preferably, no binder is used in forming the briquettes. The briquettes may be small, for instance about the size of large lima beans, or large, for instance two inches in diameter by two inches high.

The invention will be described more specifically herein with reference to the accompanying drawing which illustrates, by way of example only, a suitable apparatus for carrying out the method of the invention.

The briquettes, or alternatively a loose mixture of the powdered ingredients, are charged into an upper compartment 10 of the apparatus illustrated. In a lower compartment 11, which is in communication with the upper compartment 10, there is placed a quantity of molten salt 15 comprising one or more alkali metal halides, preferably a mixture of sodium and potassium chlorides in the weight ratio of about 2 parts sodium chloride to 3 parts potassium chloride, melting below 650° C. An atmosphere of hydrogen or other gas inert under the conditions of the process is maintained within the apparatus by introducing a stream of such gas through an inlet 12 to the upper compartment and withdrawing it through an outlet 13 at the top of the lower compartment. A tube 14 leads effluent gases and vapors from the upper compartment 10 into the body of salts 15 in the lower compartment 11. To avoid contamination of the salts 15, it is preferred to construct the tube 14 of graphite, and also to contain the salts 15 in a graphite pot 16.

The entire apparatus just described is heated, for example in a furnace 17, to a temperature sufficiently high to initiate a reaction between the ferrous chloride and silicon-zirconium-iron alloy and to maintain the salt 15 molten. The reaction will be initiated at a temperature somewhat above 200° C., usually between 220° and 250° C. The reaction is strongly exothermic and the temperature will rise rather rapidly, reaching a maximum in the neighborhood of 1100° or 1200° C. in an hour or two.

The reaction forms zirconium chloride and

some silicon chloride, both of which are volatile, the former at 331° C. and the latter at 57° C. The vapors of these chlorides pass through the tube 14 into the molten salt or salts 15. These salts dissolve the zirconium chloride and hold it in solution even at temperatures above 331° C., but do not dissolve silicon chloride at elevated temperatures. Accordingly, the silicon chloride passes out of the apparatus through the outlet 13 and the zirconium chloride remains in the salts 15. If the briquetted material contains as impurities aluminum or titanium, any chlorides of aluminum as well as any iron chlorides which may be evolved in the upper compartment and passed into the lower compartment are dissolved in the salts in the lower compartment; but titanium chlorides are not dissolved.

When a desired concentration of zirconium chloride has been attained in the molten salts 15, for instance 25% by weight, the latter are withdrawn and replaced by fresh salt.

Other salts having a higher heat of formation than zirconium chloride may be used instead of the sodium chloride-potassium chloride mixture to absorb the zirconium chloride. Very good recoveries have been obtained with for instance, a calcium chloride-sodium chloride mixture and a magnesium chloride-sodium chloride mixture, although the hygroscopicity of these mixtures is a handicap to their use. Instead of using a salt or salts to absorb the zirconium chloride, an ordinary condenser may be used. If the condenser is maintained at a suitable temperature between 57° C. and 331° C., only the zirconium chloride will be condensed.

In a typical example of the method hereinbefore described, 45.5 pounds of a briquetted mixture containing 18.25 pounds of zirconium-silicon-iron alloy and 27.25 pounds of ferrous chloride were placed in the upper compartment 10, and 26.4 pounds of a mixture of potassium chloride and sodium chloride in a weight ratio of 3 to 2 was melted in a graphite pot and placed in the lower compartment 11. The zirconium-silicon-iron alloy contained 36.8% zirconium, 47.5% silicon, remainder iron. The apparatus was heated, gas evolution started at 220° C. (measured by a thermocouple in the center of the upper compartment 10) and in 1.5 hours it reached a maximum of 1160° C. After a total of two hours, the salts were removed and were found to contain 3.61 pounds of zirconium as zirconium chloride, representing an efficiency of 53.6%. The residue in the upper compartment 10 contained 2.77 pounds of zirconium, losses and unaccounted for being only 0.36 pound or 5.4%.

According to an alternative procedure, which may be carried out in simpler apparatus, zirconium-silicon-iron alloy and iron chloride are added to a molten bath comprising one or more chlorides of metals having a high affinity for chlorine, for instance sodium, potassium, lithium, calcium, barium, or magnesium. Such dilution decreases fuming and tends to modify the violence of the reaction. A particularly useful diluent is a mixture of potassium chloride and sodium chloride in a weight ratio approximating 3 to 2. These salts do not take part in the reaction and act as solvents only; they retain the zirconium chloride but not the silicon chloride.

The molten salt bath mixture may appropriately be held between 650° and 1050° C. in a covered crucible. Within this range of temperatures the reaction is satisfactorily rapid.

Ferric chloride reacts rather violently with

high-zirconium zirconium-silicon alloys. Therefore, if the latter alloys are used, ferrous chloride is the preferred reactant, although the ferric salt may be used to react with low-zirconium alloys, with precautions against explosively violent reaction.

In a specific instance of the practice of this alternative modification of the invention, 300 parts by weight of zirconium-silicon containing 37% zirconium and about 45% silicon, remainder iron, powdered to pass a 100 mesh screen, was heated for one-half hour at 700° C. in a bath composed of 1200 parts by weight of potassium chloride and 285 parts of ferric chloride. The result was an iron-silicon sludge and a salt mixture containing as zirconium chloride 68% of the zirconium originally in the zirconium alloy. The iron content of the salt mixture was only 0.1%. Some silicon chloride was formed as a by-product and volatilized.

Most of the salt is easily separated from the iron-silicon sludge residue by decantation. The rest may be removed by vacuum distillation.

If pure zirconium chloride is desired as an intermediate or end product, it is distilled from the salt bath. Usually, zirconium metal will be desired, and this requires a further step of the process.

In the further step of the process of this invention, the molten salt mixture containing zirconium chloride resulting from the first step, as practiced by either of the alternatives described, is contacted with metal of the group consisting of the alkali metals, the alkaline earth metals, and magnesium, a preferred reagent for this step being magnesium. These metals, having a far greater affinity than zirconium for chlorine, replace the zirconium in the chloride and precipitate zirconium in powdered form. After the reaction, most of the salt is decanted for reuse, the resulting mixture of zirconium and salt is cooled and broken up, and the salt is removed by vacuum distillation or by washing with water. The reaction will readily go practically to completion, leaving only a very low concentration of zirconium chloride which may be recycled.

We claim:

1. Process for producing zirconium chloride which comprises reacting solid ferrous chloride and solid zirconium-silicon alloy, in the absence of other chlorinating agents, at a temperature above the volatilization temperature of the chlorides of silicon and zirconium and in the range 220° C. to 1200° C., but for a substantial period of time not rising above the volatilization temperature of ferrous chloride, so as to produce a mixture of the vapors of zirconium chloride and silicon chloride and then passing the mixture into molten alkali metal chloride which dissolves only the zirconium chloride.

2. Process for producing zirconium chloride which comprises reacting a briquetted mixture of comminuted solid ferrous chloride and comminuted solid zirconium-silicon-iron alloy, in the absence of other chlorinating agents, at a temperature above the volatilization temperature of the chlorides of silicon and zirconium and in the range 220° C. to 1200° C., but for a substantial period of time not rising above the volatilization temperature of ferrous chloride, so as to produce a mixture of the vapors of zirconium chloride and silicon chloride and then passing the mixture into molten alkali metal chloride which dissolves only the zirconium chloride.

3. Process for producing zirconium chloride

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which comprises reacting a briquetted mixture of comminuted solid ferrous chloride and comminuted solid zirconium-silicon-iron alloy, in the absence of other chlorinating agents, at a temperature above the volatilization temperature of the chlorides of silicon and zirconium and in the range of 220° C. to 1200° C., but for a substantial period of time not rising above the volatilization temperature of ferrous chloride, so as to produce a mixture of the vapors of zirconium chloride and silicon chloride and then passing the mixture into a molten mixture of sodium and potassium chloride which dissolves only the zirconium chloride.

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