

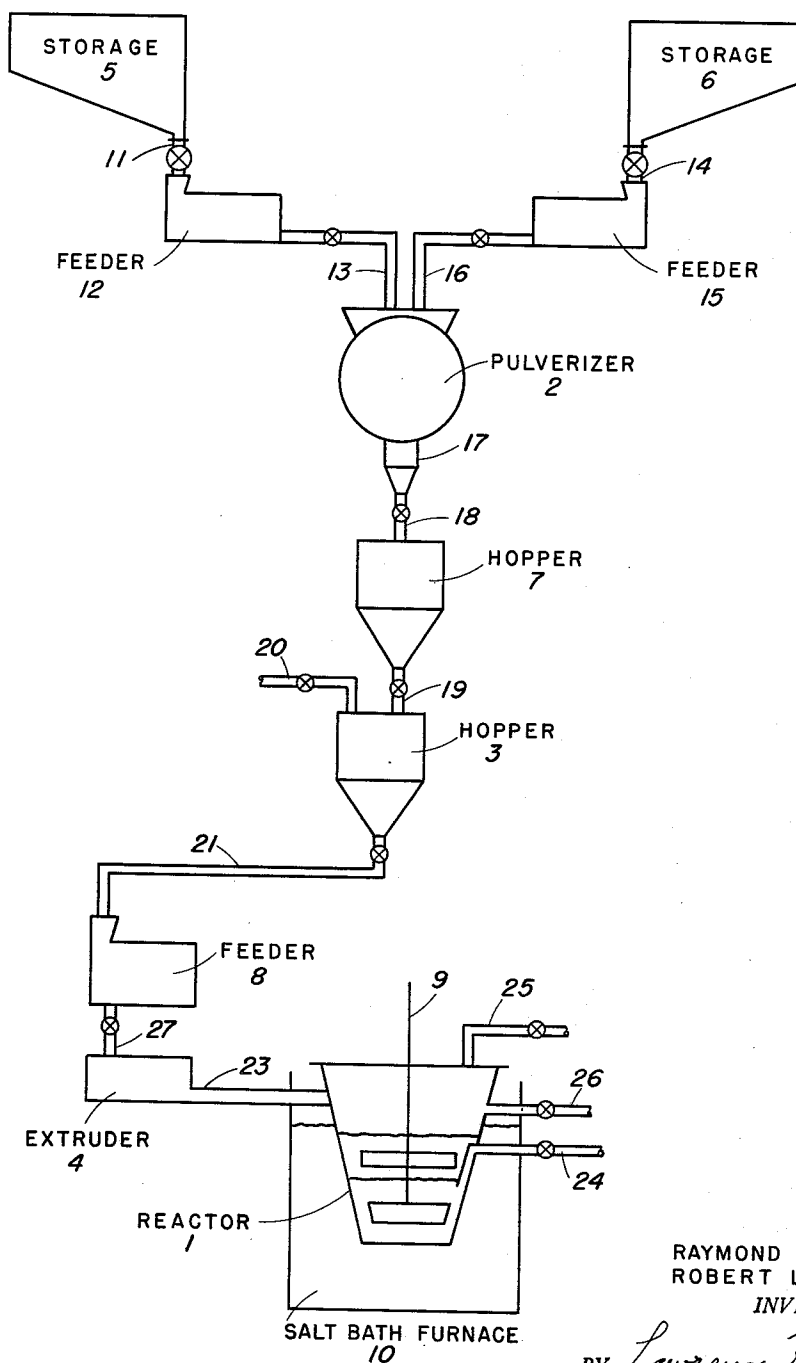
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R. A. FOOS ET AL

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METHOD OF PRODUCING COLUMBIUM AND TANTALUM

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RAYMOND A. FOOS
ROBERT L. MADDOX
INVENTORS

BY *Lawrence Rosten*
ATTORNEY

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METHOD OF PRODUCING COLUMBIUM AND TANTALUM

Raymond A. Foos and Robert L. Maddox, Cincinnati, Ohio, assignors to National Distillers and Chemical Corporation, New York, N.Y., a corporation of Virginia

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This invention relates to a new and improved process for the preparation of metals. More particularly, the invention pertains to a continuous process for the production of columbium and tantalum metals and mixtures thereof by reduction of the double fluoride salts of these metals.

In recent years there has been considerable interest in the production of high purity columbium and tantalum metals. Many of the processes heretofore proposed for commercial application first prepare the double fluoride salts of these metals, and then subject these salts to a reduction treatment in order to yield the desired metal product. For example, in one process directed to the preparation of columbium or tantalum metals the double fluoride salts have been electrolytically reduced. This process is, however, quite costly, and many of the recently proposed processes attempt to provide more economical methods. One such method is the chemical reduction of the double fluoride salts with known reducing agents such as metallic sodium, etc. However, this method has the disadvantage of being essentially a batch-type operation which requires elaborate reactor preparation and spalt removal systems.

It is one object of this invention to provide a process for recovering the metals from their double fluoride salts which avoids the problems encountered in the prior art methods. Another object of this invention is to provide a chemical reduction process which can be operated continuously independent of scale with the production of outstanding yields of high quality metal products.

These and other objects of the invention are attained by utilizing a carefully controlled reduction process involving the reaction of the double fluoride salts of columbium and tantalum with a reducing agent under prescribed operating conditions. In general, the process comprises the steps of comminuting or pulverizing the double fluoride salt reactant, degassing and dehydrating the comminuted salt and then mixing the so-treated salt with a molten reducing agent such that all reactants are contacted in a liquid media under certain specific conditions to effect a continuous reduction reaction with continuous recovery of finely divided metal product. In accordance with another aspect of this process, an alkali metal halide salt may be comminuted along with the double fluoride salt to ensure the production of high yields of quality metal. Other important features of the invention will be described in detail hereinafter.

The double fluoride salts which may be employed in the process of this invention will correspond to the following structural formula:



wherein R is an alkali metal such as sodium, potassium or lithium, and M is columbium or tantalum.

The reducing agents capable of being utilized in the process will include sodium, potassium and lithium. As previously discussed, the use of a reducing agent which is fluid in the reaction mixture is an important feature of the invention, and the use of molten sodium as the reductant is especially preferred. In carrying out the reduction of the double fluoride salt, it is desirable to control the amount of reducing agent employed to ensure

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that substantially stoichiometric amounts are fed into the reaction zone. In accordance with the preferred operation, a small excess of the reducing agent is employed.

The inert salt diluent which may be employed in conjunction with the double fluoride salt reactant can be an alkali metal halide salt such as sodium and potassium chlorides, bromides and iodides. The amount of diluent salt utilized is not critical, though preferably a 1:1 ratio of diluent salt to double fluoride will be provided.

For a more complete understanding of this invention, reference will now be made to the drawing which is a schematic showing of one form of the apparatus wherein the process may be carried out. However, it will be readily apparent that this particular embodiment may be varied without departing from the scope of this invention.

Referring now to the drawing, there is shown a storage hopper 5 for the double fluoride salt, which is fed via line 11, gravimetric feeder 12, and line 13 into pulverizer 2. When diluent salt is employed in the process it will be passed from storage hopper 6 via line 14, gravimetric feeder 15 and line 16 to pulverizer 2 concurrently with the continuous flow of double fluoride salt. The storage units and the gravimetric feeders may be conventional equipment. Pulverizer 2 may also be any such equipment which will pulverize or comminute the salt feed to an average particle size of less than about 100 mesh, preferable about 100 to 325 mesh.

The pulverized double fluoride salt and the diluent alkali metal halide salt, when employed, recovered from pulverizer 2 is passed via conduit 17 and line 18 to hopper 7 where it accumulates as a heel such that the vacuum maintained in hopper 3 will not pull any gases or vapors through the retained bed of pulverized material. From hopper 7 the pulverized salt is fed via line 19 to hopper 3 where it is heated to a temperature of about 100° to 400° C., preferably about 150° to 300° C., while the gases and vapors in hopper 3 are evacuated via line 20 to maintain substantially vacuum conditions in this hopper. In this step the water and any absorbed gases are removed from the pulverized salt feed.

The dehydrated pulverized double fluoride salt is discharged from hopper 3 via line 21 into gravimetric feeder 8, from where it passes via line 27 into extruder 4. The extruder forces the pulverized material through a die plate to produce dry powdery pellets. The size of the pellets will be determined by the particular die plate employed and the amount of compaction obtained. For practical purposes, however, the pellets will have an outside diameter of about 1/8 to 1/2 inch and a length of about 1/2 to 1 inch, although these sizes are not critical. The salt pellets are transported through barrel 23 of extruder 4 to reaction vessel 1. It will be understood that the reactor may be of conventional design. However, in order to more fully illustrate the invention, a conical reaction vessel 1 is shown in the drawing. The reaction vessel is internally lined with nickel or a suitable non-alloying material, and is 18 inches deep with an internal diameter of 16 inches at top and an internal diameter of 12 inches at the bottom. A nickel stillwell 24, having an internal diameter of 0.5 inch, extends through the reactor vessel wall 12 inches from the bottom of the reactor, and is positioned in a downward direction, parallel and against the reactor wall to a depth of 5 inches. Reaction vessel 1 is also provided with stirrer 9 which is of pitched blade design but may also be of any conventional design. As shown in the drawing, reaction vessel 1 is positioned in a gas-fired salt bath furnace 10, which is employed to heat the reactor to temperatures within the range of about 200° to 1000° C., preferably about 800° to 900° C., though only a temperature sufficient to maintain a molten reaction medium need be employed. Other methods of heating reaction vessel 1 such as direct heating may be

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utilized. The materials employed in the salt bath furnace comprise sodium chloride, potassium chloride, lithium chloride, barium chloride, sodium fluoride, potassium fluoride, lithium fluoride and mixtures thereof.

The molten reducing agent will be metered into the top of reaction vessel 1 via line 25. In accordance with another feature of the invention, an inert gas atmosphere of about 1 to 10 p.s.i.g. is maintained in the reactor, at all times. Neon, argon, etc. and mixtures of these and other inert gases may be employed for this purpose. The inert gas is passed into reaction vessel 1 via line 26.

In carrying out the process of the invention the pulverized double fluoride salt, either alone or in admixture with the aforementioned inert salt diluent, is fed continuously in controlled amounts to a reaction zone concurrently with a flow of molten reducing agent, e.g. sodium. The reaction product mixture which comprises finely divided heavy metal particles is maintained under continuous agitation by rotating stirrer 9 at about 70 to 750 r.p.m. and is continuously withdrawn from the reaction zone via line 24 for separation of the desired metal product from the by-product salts.

Referring again to hopper 3, sufficient pulverized salt or salt mixture bed will be maintained in the hopper so that no air or other gas vapors will gain entrance by passing through the bed. Since this same condition exists in hopper 7, the evacuated space within hopper 3 can be maintained at as low a vacuum as is necessary. In addition, it will be understood that both hoppers may be equipped with such conventional devices as stirrers, bridge-breakers, etc. as is required in order to maintain movement of the powdered salt or salt mixtures into the entrance port of their respective discharging devices. With reference to discharge line 24 in reaction vessel 1 it will be understood that any effective overflow spout may be employed. The discharge line is preferably so situated and equipped with a baffled entrance so that the reaction product mixture entering its opening has been contacted with sufficient reducing agent to minimize the amount of unreacted double fluoride salts withdrawn. The actual discharging can be effected either by maintaining a positive pressure, derived from the atmosphere of inert gas, above the liquidus level in the reactor or by utilizing the force of gravity such as by positioning the terminal ending of the discharge pipe at a sufficiently lower level than the level of the liquidus.

The invention will be more fully understood by reference to the following illustrative embodiments, which are carried out in the apparatus described in the drawing:

Example I

K_2TaF_7 , which has been previously comminuted and outgassed, is metered gravimetrically at a rate of 3.40 lb./min. from the gravimetric feeder ahead of the extruder. The extruder passes the powdered salt into the reactor, heated at 900° C. Simultaneously with this stream of compacted salt, molten sodium is metered into the reactor at a 1 lb./min. rate. Both materials are contacted with molten KF and NaF in which is suspended tantalum metal particles produced from previous operations with agitation, and they react together to produce particles of tantalum metal and molten KF and NaF. A proportionate quantity (volumewise) of the reaction product mixture of NaF, KF and Ta is displaced from the reactor via the stillwell and empties continuously into a suitable receiver at a rate of 4.40 lbs./min. of slurry, containing 36% tantalum metal by weight.

Example II

K_2TaF_7 and KCl are metered gravimetrically from separate metering stations at a rate of 3.44 lbs./min. each. The streams are joined at a single runner disc mill and comminuted, with some degree of mixing occurring, to <100 mesh. This mill discharge material is transported, successively through a surge bin evacuation hopper heated at 150° C. Here some weight is lost due to

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outgassing of water and residual gases. The evacuation hopper contents are stirred continuously to effect good mixing and outgassing of its charge. A blended stream of salts is discharged into a surge bin. The rate of discharge from the evacuation hopper is regulated by a level controller. The material is emptied from the surge bin by another gravimetric feeder station at a rate of 6.80 lbs./min. into an extruder. The extruder compacts and feeds the salt compresses into the reactor, heated at 800° C. Simultaneously, molten sodium is metered at a rate of 1 lb./min. Contacting of reactants by agitation results in the formation of very fine particles of tantalum metal suspended in a liquid mixture comprising molten KF, NaF and KCl. The reaction by-products overflow via a stillwell into a suitable receiver at a rate of 7.8 lbs./min. containing 20% Ta.

In accordance with another aspect of the invention, various metal alloys may be prepared by this process. More specifically, mixtures of two or more alkali metal-heavy metal fluoride salts may be treated by the present method to produce alloys of the heavy metals. Thus, a mixture of the columbium and tantalum double fluoride salts may be advantageously employed to prepare columbium-tantalum alloys of varying compositions. It is also possible to use the alkali metal salt in such a process, if desired. Other than utilizing mixtures of double fluoride salts as the feed material, the process will be the same as described above. This is more fully illustrated in the following embodiment:

Example III

Instead of charging one of the metering stations with KCl as was done in Example II, K_2CbF_7 is charged and fed in exactly the same manner at a rate of approximately 1.38 lbs./min. This joins a stream of metered K_2TaF_7 (1.75 lbs./min.) and this mixed stream is further processed as described in Example II. The compressed outgassed salts are extruded into a reactor at 900° C., at a total rate of 3.04 lbs./min. which is 35% wt. Cb and 65% wt. Ta in composition. Simultaneously, 1 lb./min. of molten sodium is metered into the reactor. Reduction of these metal fluoride salts occurs instantaneously at these conditions when contacted, by means of agitation, with sodium. The resultant slurry, consisting of particles of Cb-Ta metal and molten KF and NaF overflows from the reactor into a receiver at a rate of 4.04 lbs./min.

In accordance with one method of starting up the process of this invention, a portion of the double fluoride salt or mixtures of such salts may be charged to reactor 1, and then heated under vacuum to a temperature of about 300° C. or higher with stirring. An inert gas such as argon is introduced into the reactor to maintain an inert atmosphere of about 5 p.s.i.g. After the reactor has been heated to a temperature of about 800° C., a substantially stoichiometric amount of molten sodium is added to the reactor. The reactor is then continuously charged with fresh reactants, with or without a salt diluent, to commence the desired operations. As set forth above, a liquidus of reaction products will be maintained in reactor 1 to serve as the reaction medium.

While particular embodiments of this invention are shown above, the invention is obviously subject to variation and modification without departing from its broader aspects. For example, the alkali metal-heavy metal fluoride salt feed material may be prepared in accordance with any known process. It will be understood, therefore, that these and other modifications may be employed within the scope of the foregoing description of the invention and the following claims.

What is claimed is:

1. A continuous method for producing a metal selected from the group consisting of columbium and tantalum from a double fluoride salt thereof having the formula



wherein R is an alkali metal and M is the selected metal,

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which comprises continuously and simultaneously feeding said double fluoride salt, in solid form, and a molten alkali metal reducing agent into a reaction zone and into molten products of reaction between said double fluoride salt and said reducing agent contained in said reaction zone, said molten products of reaction being maintained at a temperature of about 200° to 1000° C., and continuously removing a portion of the reaction product mixture containing the selected metal from said reaction zone.

2. The method of claim 1 wherein M is columbium.

3. The method of claim 1 wherein M is tantalum.

4. The method of claim 1 wherein R is potassium.

5. The method of claim 1 wherein said molten reducing agent is sodium.

6. The method of claim 1 wherein said double fluoride salt is ground to an average particle size of less than about 100 mesh and degassed prior to being fed into the reaction zone.

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7. The method of claim 1 wherein a mixture of tantalum- and columbium-alkali metal fluoride salts is fed into the reaction zone to produce columbium-tantalum alloys.

8. The method of claim 1 wherein an inert alkali metal halide salt is continuously fed into said reaction zone with the double fluoride.

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