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PRODUCTION OF AN ALKALI METAL DOUBLE FLUORIDE OF ZIRCONIUM OR HAFNIUM

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Zirconium metal may be made conveniently in pure form by the electrolysis of a fused salt consisting of a solution of an alkali double fluoride of zirconium in an alkali halide, the preferred alkali halide being sodium chloride. In view of the high cost of the fluoride derivative of zirconium, the process is to a certain extent academic when compared with other methods for production of pure metal. Unless adequate means are available for recovery of the valuable fluoride chemicals, it would not be possible to reduce the cost of preparation of the metal into a useful commercial range. In view of the very useful properties of zirconium metal, a considerable effort has been expended in search for low cost methods of production of the metal. Through use of the electrolytic decomposition of the type of fused salt baths indicated in the foregoing, I have now found that it is possible to eliminate the losses heretofore supposed to be inevitable and have developed a procedure whereby a pure product can be obtained at a cost which makes the process commercially attractive. I have accomplished this novel result by finding means to recover the fluorine chemicals quantitatively as a by-product and recycling these recovered fluorine chemicals back through the process so that none of this reagent is lost. Other objects and advantages will appear from the following description.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In the electrolysis of a fused salt consisting of a mixture of the alkali double fluoride of zirconium and sodium chloride, the reaction is carried out by adding the zirconium compound as needed to make up for zirconium metal being deposited at the cathode. The products of the electrolytic reaction are zirconium metal at the cathode and chlorine gas at the anode. Thus the fluoride content of the bath increases continually. Usually the starting mixture consists of 16 mole per cent potassium zirconium fluoride and 84 mole per cent sodium chloride. The electrolysis is normally continued until the sodium chloride content is reduced to a range covering 6 to 10 per cent so that for all practical purposes the bath composition at this point consists of a mixture of the fluorides and chlorides of sodium and po-

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tassium. As described in my copending application, Serial No. 269,146, filed January 31, 1952, I have developed a novel means for decomposing ores of zirconium, involving the presence of water soluble fluorides such that the end product of this novel decomposition reaction is the preparation of pure potassium zirconium fluoride. I have now found that I may use the spent bath materials resulting from the electrolysis of the complex zirconium salt as a starting raw material for decomposition of fresh zirconium ore. In this way, the fluoride content from the spent bath is then recovered quantitatively through the medium of preparation of the desired starting compound for the electrolysis itself. On this basis, then, the process becomes completely cyclic with respect to the fluoride chemicals and the major item of cost normally presented when these fluoride chemicals were discarded is thus bypassed or eliminated. Obviously this cyclic recovery of fluorine chemicals is a major advance relative to the economics in consideration of this particular electrolytic method for the preparation of zirconium metal.

As raw material for production of metal in accordance with the present process, zirconium-containing compounds or ores of silicate, oxide and other operable character are employed. Usually, a preferred raw material is zirconium silicate. The zirconium-containing raw material is first subjected to a sintering or calcining reaction with an alkaline earth compound. Preliminarily, the ore is finely ground, such as desirably to -325 mesh, and after being then mixed with an alkaline earth compound which can form an insoluble sulphate, e. g., a compound of calcium, barium or strontium, and preferably from the standpoint of economics, limestone or calcium carbonate, of similar fineness. The latter may be in the proportion desirably of a mole of limestone per mole of zirconia and one mole of limestone per mole of silica. In general the requirement is that the molar sum total of zirconia and silica be stoichiometrically equivalent to the limestone. Besides limestone, calcium chloride is also included in amounts equivalent to about 10 molar per cent of the amount of limestone. The mixed materials, ground together, are calcined to a sintering temperature, for instance around 1310° C. for about one hour, or for a longer period of time at temperatures as low as 1200° C. and in general the desirable conditions are a temperature range of 1200-1310° C. for periods of one to three hours. A semi-muffle furnace or a rotary kiln may be used for this. After the calcining or sin-

tering operation, the material is cooled and finely ground, as to about —325 mesh.

The complex formed by the foregoing operation is then slurried in water, usually about one part by weight of solid to 5 parts of water. Then, concentrated sulphuric acid is added in definite amounts as rapidly as possible and a vigorous exothermic reaction occurs, resulting in evolution of steam and in solidification of the slurry. The amount of water should be adjusted such that the reaction does not go to complete dryness. After cooling, the gelatinous mass is broken up in water added to a stirrable suspension. By vigorous stirring for several minutes the material is well disseminated, and then water-soluble fluorides are added, these being of the alkali class, potassium, sodium and ammonium, and one or more chlorides similarly may be included. Double fluorides of zirconium and a selected alkali metal are made. To form potassium zirconium fluoride, a desirable fluoride addition is 2 moles of potassium fluoride and 4 moles of sodium fluoride; or if desired, 6 moles of potassium fluoride may be used per mole of the prepared calcium zirconium silicate complex. The fluorides are added in solution, fairly concentrated.

As afore-indicated, all the fluorine requirements are supplied from the spent bath constituents resulting from the electrolysis and the amount of such constituent to be used is determined by the fluorine content in relation to the potassium ion content such that the combination of the two is sufficient to form the compound K_2ZrF_6 . A variety of modifications of bath composition may be used which modify the course of these calculations. For example, the preferred bath is a mixture of potassium zirconium fluoride and sodium chloride. In this case, the spent composition will consist of mixtures of the fluorides and chlorides of sodium and potassium. Another bath which is conveniently used will consist of a mixture of potassium zirconium fluoride and potassium chloride, while in a third case the bath may consist of a mixture of sodium zirconium fluoride and potassium chloride, and so forth. In each case, therefore, the amount of spent bath to be used is determined as the result of chemical analysis in order to insure that all the fluorine is recovered and that sufficient potassium ion is available to precipitate the desired compound. In those cases where no potassium ion is present, the desired sodium zirconium fluoride is obtained by evaporative techniques from the various solutions. In adding these spent constituents as initial starting raw reagents, it has been determined that the amount of chlorine ion which normally remains in the spent bath as the result of the continuation of the electrolysis does not have an adverse effect on the formation of the desired zirconium compound.

The amount of sulphuric acid depends to some extent on the constitution of the reactants. One mole of sulphuric acid per each mole of lime present is required, and in addition sufficient acid to combine with all the alkali which does not go into the preparation of the double potassium zirconium fluoride. A slight excess of soluble fluoride ion is added to insure quantitative crystallization of the potassium zirconium fluoride.

The reaction with the fluoride is preferably carried out with the material maintained at a temperature of 90–100° C. After the fluoride has all been added, sufficient water is further added to maintain all of the potassium zirconium

fluoride in solution. This normally involves an amount of water about 4 to 5 times that of the weight of the potassium zirconium fluoride being made. If the raw material has an iron content, it is necessary to make certain that all of the iron is in the ferrous form, and this may be accomplished by reduction with scrap iron in the acid solution. The iron precipitates as hydrate and is eliminated as an insoluble residue. A precipitate of alkaline earth sulphate or calcium sulphate and silica is formed, and potassium zirconium fluoride remains in solution at the elevated temperature. The precipitated matter is separated by decanting or filtration, and the potassium zirconium fluoride is recovered from the solution by crystallization. Addition of a small amount of potassium chloride also gives quantitative separation of the desired compound. Instead of sulphuric acid, any acid which forms an insoluble alkaline earth precipitate, viz., phosphoric acid, etc., may be employed. For crystallization of the potassium zirconium fluoride, evaporation until the first signs of crystals appear, and then cooling, gives the desired result.

The reactions and procedures afore-described with respect to zirconium, also similarly apply to hafnium.

The double fluoride is next decomposed to form the desired zirconium metal or hafnium metal, and while this may be effected by thermal reaction, it is generally preferable to electrolyze the material. This decomposition is carried out under an inert atmosphere, and the double fluoride is electrolyzed in a molten bath of sodium chloride, this being preferred over other alkali or alkaline earth halides. The electrolytic decomposition is carried out at a temperature between 800 and 1000° C. A voltage of 3 to 8 is used, and current densities of 50 to 400 per square decimeter of cathode. Thus with an inert atmosphere of argon, helium or the like, electrolysis is carried on, and fresh portions of the potassium zirconium fluoride are added as the electrolysis continues, up to the point where the chlorine ion content is less than 10 per cent of the total. The zirconium or hafnium metal having been deposited at the cathode, the residual alkali fluoride and chloride of the bath is returned or recycled to the stage of formation of double fluoride as above referred to. The presence of the chloride does not interfere. The material returned or recycled to the zone operating on fresh zirconium ore to form double fluorides, accordingly involves ions which may be of potassium and sodium and fluorine and chlorine, or of potassium and fluorine and chlorine, or of sodium and fluorine and chlorine; i. e., in any case ions of fluorine and chlorine and of alkali metal whose atomic weight is at least as high as sodium and not greater than potassium.

The following examples are illustrative of the process:

Example 1.—A beneficiated zirconium silicate beach sand is ground to —325 mesh and 185 parts by weight of this is mixed with 200 parts of calcium carbonate and 25 parts of anhydrous calcium chloride, and the mixture is re-ground. It is then fed into a rotary kiln at a temperature of 1310° C., and the material is calcined to a sinter, being subjected to the heat for about an hour. It is discharged and cooled, and the calcine is ground to about —325 mesh, and is slurried in about 800 parts of water. Sulphuric acid of 98 per cent grade is added in amount of about 410 parts by weight, and vigorous stirring is contin-

ued until the temperature begins to rise. The stirring is then stopped and the reaction allowed to continue as an exothermic reaction with evolution of steam, and formation of a crumbly slightly gelatinous mass. This is then mixed with 2000 parts of water and is stirred until thoroughly broken up. 325 parts of spent electrolytic bath is dissolved in 1500 parts of boiling water. The analysis of this spent bath reduced to ion species is as follows: 33.2% Na+, 24.8% K+, 36.4% F-, 5.6% Cl-. This is stirred into the slurry which is heated to a temperature of 90 to 100° C. After all fluoride is added, digestion is continued at such temperature for about an hour, and then the solution is allowed to settle quietly. The clear liquid is decanted, and the granular residue is washed on a filter with hot water containing 1 per cent of sulphuric acid and 1 per cent of potassium fluoride. This wash liquid is combined with the decant, and 10 parts by weight of potassium chloride in 50 parts of water are added, and the liquid is evaporated until crystallization starts. The liquid is then discharged to a crystallizing pan and cooled. The crop of crystals is centrifuged, and may be washed one or more times with water containing potassium fluoride or chloride, and is dried at about 100° C. A yield of 275 grams of anhydrous potassium zirconium fluoride is obtained. This double fluoride is then electrolytically decomposed, 10 to 35 per cent of the double zirconium fluoride being added to sodium chloride 65 to 90 per cent of the bath. Electrolysis is carried on at a temperature of about 900° C. and voltage about 6 and current 300 amp. per square decimeter at the cathode, fresh portions of the double fluoride being fed in progressively, until the chlorine content of the molten bath falls below about 10 per cent. Then the bath residue, involving otherwise waste fluoride and chloride, is returned or recycled to the sulphuric acid digestion stage for more double fluoride formation.

Example 2.—Same as in Example 1 except that the spent fluoride containing material for recycling is obtained from a bath which consists of a mixture of sodium zirconium fluoride and sodium chloride. In this particular case, 295 parts of spent bath is dissolved in 1500 cc. of water. The analysis of this spent bath is as follows: 53% Na+, 41% F-, and 6% Cl-.

Example 3.—Same as in Example 1 except that the electrolytic bath from which the zirconium made consists of a mixture of potassium zirconium fluoride and potassium chloride. In this case, 395 parts of the spent bath is dissolved in 1500 cc. of water. The analysis of the spent bath in this case is as follows: 66% K+, 30% F-, and 4% Cl-.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I therefore particularly point out and distinctly claim as my invention:

1. The method of producing an alkali metal double fluoride of a refractory metal of the group consisting of zirconium and hafnium which comprises heating an aqueous solution of a compound of the refractory metal to a temperature of at least 90° C. in the presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal double fluoride of said refractory metal in a fused alkali

metal chloride bath, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal double fluoride of the refractory metal.

2. The method of producing an alkali metal double fluoride of a refractory metal of the group consisting of zirconium and hafnium which comprises heating an aqueous solution of a compound of the refractory metal to a temperature of at least 90° C. in the presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal double fluoride of said refractory metal in a fused alkali metal chloride bath, said spent salt bath containing not more than about 10% by weight of chlorine in the form of residual alkali metal chloride, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal double fluoride of the refractory metal.

3. The method of producing an alkali metal double fluoride of a refractory metal of the group consisting of zirconium and hafnium which comprises heating an oxidic compound of the refractory metal in admixture with an oxidic alkaline earth metal compound to a sintering temperature with the resulting formation of the corresponding alkaline earth metal oxy-salt of the refractory metal, digesting said oxy-salt in sulfuric acid, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal double fluoride of said refractory metal in a fused alkali metal chloride bath, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal double fluoride of the refractory metal.

4. The method of producing an alkali metal double fluoride of a refractory metal of the group consisting of zirconium and hafnium which comprises heating an oxidic compound of the refractory metal in admixture with an oxidic alkaline earth metal compound to a sintering temperature with the resulting formation of the corresponding alkaline earth metal oxy-salt of the refractory metal, digesting said oxy-salt in sulfuric acid, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal double fluoride of said refractory metal in a fused alkali metal chloride bath, said spent salt bath containing not more than about 10% by weight of chlorine in the form of residual alkali metal chloride, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal double fluoride of the refractory metal.

5. The method of producing an alkali metal fluozirconate which comprises heating an aqueous solution of a zirconium compound to a temperature of at least 90° C. in the presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal fluozirconate to zirconium metal in a fused alkali

metal chloride bath, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal fluozirconate.

6. The method of producing an alkali metal fluozirconate which comprises heating an aqueous solution of a zirconium compound to a temperature of at least 90° C. in the presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal fluozirconate to zirconium metal in a fused alkali metal chloride bath, said spent salt bath containing not more than about 10% by weight of chlorine in the form of residual alkali metal chloride, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal fluozirconate.

7. The method of producing an alkali metal fluozirconate which comprises heating an oxidic zirconiferous material in admixture with an oxidic alkaline earth metal compound to a sintering temperature with the resulting formation of the corresponding alkaline earth metal zirconate, digesting said zirconate in sulfuric acid, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal fluozirconate to zirconium metal in

a fused alkali metal chloride bath, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal fluozirconate.

8. The method of producing an alkali metal fluozirconate which comprises heating an oxidic zirconiferous material in admixture with an oxidic alkaline earth metal compound to a sintering temperature in the further presence of a small amount of an alkaline earth metal chloride with the resulting formation of the corresponding alkaline earth metal zirconate, digesting said zirconate in sulfuric acid, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of a source of fluoride ions and of alkali metal ions consisting essentially of the spent salt bath resulting from the electrolytic decomposition of an alkali metal fluozirconate to zirconium metal in a fused alkali metal chloride bath, effecting separation from the resulting aqueous phase of any insoluble phase, and crystallizing from said separated aqueous phase the resulting alkali metal fluozirconate.

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