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PROCESS FOR THE CONCURRENT PRODUCTION OF AlF_3 AND A METALLIC TITANIUM PRODUCT

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ABSTRACT OF THE DISCLOSURE

AlF_3 and a metallic titanium product (Ti, Al-Ti alloys, or both) are produced by reducing TiF_4 with metallic aluminum. The reaction environment is essentially anhydrous. Elevated temperatures are generally used. The reaction may be effected in a suitable solvent (e.g., pyridine) or the reactants may be combined in the absence of a diluent and reacted at a suitable elevated temperature. AlF_3 may be separated from the titanium product by physical procedures (e.g., extraction with deaerated water).

Background of the invention

This invention relates to the production of metallic titanium products. More particularly this invention relates to a thermochemical process for concurrently producing aluminum fluoride and metallic titanium, aluminum-titanium alloys, or mixtures thereof.

Various processes involving thermochemical reduction of titanium compounds (chiefly the halides and oxides) as a means of preparing titanium or titanium alloys are known (e.g., U.S. Patents 1,533,505, 1,602,542, 2,267,-298, 2,618,549, 2,618,550, 2,663,634, 2,708,158, 2,803,-536, 3,062,641).

Perhaps the best known process is that described by Kroll (U.S. 2,205,854) which in preferred form involves reducing titanium tetrachloride with magnesium at a temperature ranging from 800 to 1070° C. in a protective atmosphere.

A potentially useful reducing metal for a Kroll-type process because of its low cost, commercial availability and high purity is aluminum. However so far as is known, the art makes no reference to reducing titanium tetrachloride with metallic aluminum. Moreover thermodynamic calculations tend strongly to indicate that the desired reaction will not proceed:

$$TiCl_4 + \tfrac{1}{3}Al \xrightarrow{200°C.} TiCl_3 + \tfrac{1}{3}AlCl_3$$

$$T_iCl_3 + Al \longrightarrow Ti + AlCl_3;\ \Delta F_{25°C.} = +1.2\ Kcal.$$

Other background disclosures of which we are aware include the following:

Kroll (supra).—"Of the titanium halides applicable, tetrachloride ($TiCl_4$) particularly is of practical value. The fluorides are all solid and therefore cannot be readily introduced into the reaction chamber. The alkaline earth fluorides resulting therefrom are insoluble in water and are therefore difficult to be eliminated according to the wet process." (Page 2, column 1, lines 49–55.)

"Finally, in some cases where it is possible to form an alloy, an alloy of the alkaline earth metals may be employed, such as, for instance, calcium aluminum, in which case aluminum titanium is produced. * * * However, this method is, as a rule, not so suitable, since said alloys may be produced with a greater certainty by direct fusion or by sintering." (Page 2, column 2, lines 51–62.)

Olson (U.S. 2,753,256).—"As already noted, other metal reducing agents, and particularly aluminum, may

be employed in the process. Aluminum dissolves readily in zinc and gives a reagent which readily reacts with titanium tetrahalides, particularly $TiCl_4$. Aluminum chloride is formed as a gas under the existing conditions which may be led from the system and separated from titanium tetrachloride by resort to the usual physical means." (Page 2, column 4, lines 24–31.)

"Obviously, titanium tetrachloride is the commercially preferred utilizable halide of titanium, but other titanium halides, such as the bromides or iodides, may be substituted for use, if desired and economically available." (Page 3, column 5, lines 11–15.)

Kamlet (U.S. 2,781,261; 2,837,426) refers to work of Manchot et al. on forming titanium-aluminum alloys by reacting potassium fluotitanate with metallic aluminum and to his own work on this type of process as described in his U.S. 2,785,971. As Kamlet brings out in his latter two patents (supra) the starting material—the alkali metal fluotitanate—is not a common article of commerce. These two patents describe certain reaction sequences for regenerating alkali metal fluotitanate from the byproducts of the described reactions.

Singleton (U.S. 2,766,111) discloses reducing titanium tetrachloride vapors to titanium metal by reacting these vapors with vapors of aluminum monochloride. The patentee states (page 1, column 1, line 71–column 2, line 3):

"The reaction zone is preferably maintained at a temperature above about 1200° C. so as to prevent disproportionation of the introduced aluminum monochloride to aluminum and aluminum trichloride."

The patentee also states (page 3, column 5, lines 59–65):

"In general it can be stated that the reaction between aluminum monofluoride and titanium tetrafluoride is more favorable, from a thermodynamic standpoint, than the reaction involving the corresponding chlorides. However, the additional cost of the halogen and the problems of corrosion with fluorine compounds is such as to make the use thereof less desirable."

Summary of the invention

An object of this invention is to provide a process for preparing titanium or titanium-aluminum alloys or both which (a) uses as a source of titanium, a titanium halide which can be readily produced from economical, readily available raw materials, (b) uses as the reductant metallic aluminum of relatively high purity, a material widely available as an article of commerce, (c) produces a desirable aluminum-containing byproduct and (d) is capable of being practiced at relatively low temperatures.

Other objects of this invention will be apparent from the ensuing disclosure and appended claims.

In accordance with this invention aluminum fluoride and a desirable metallic titanium product (titanium or aluminum-titanium alloys or both) are concurrently produced by reacting titanium tetrafluoride with metallic aluminum in an essentially anhydrous environment and at a temperature sufficiently high and for a period of time sufficienutly long to effect complete chemical reduction of at least a portion of the titanium fluoride. Hence this process utilizes simple, relatively low cost reactants. Titanium tetrafluoride is readily prepared from titanium tetrachloride and HF (e.g., see Sidgwick, "Chemical Elements and their Compounds," Oxford, 1950, volume I, page 637). Metallic aluminum of excellent purity is a ubiquitous material.

Description of the preferred embodiments

One embodiment of this invention involves carrying out the above reaction in an organic reaction medium in

which the titanium tetrafluoride is soluble. A number of suitable media are available for this use, the chief criteria being that at the reaction temperature employed they should be chemically stable and in the liquid state. Exemplary of suitable reaction media for use in this embodiment of the invention are pyridine and certain suitably substituted pyridine derivatives.

Another embodiment involves conducting the present process in the absence of an organic reaction medium. This may be accomplished by reacting titanium tetrafluoride with molten aluminum in an otherwise inert reaction system (i.e., under a suitable protective atmosphere). For example titanium tetrafluoride may be introduced into a system containing molten aluminum. Conversely finely-divided aluminum droplets may be introduced into a heated reaction zone containing particulate titanium tetrafluoride in a suspended or agitated state, or titanium tetrafluoride in the gaseous state.

Still another embodiment of the invention is to form a premix of titanium tetrafluoride and finely-divided aluminum which is then heated in an inert environment to a reaction temperature below the boiling point of titanium tetrafluoride at the reaction pressures employed. These and other ways of practicing the process will now be apparent to those skilled in the art.

Essentially pure metallic aluminum is utilized in the present process. This avoids undue contamination of the metallic titanium product by impurities which would otherwise be introduced into the system by means of the aluminum. Thus for most purposes the aluminum reductant should have a purity of at least about 99.5 percent, the balance being conventional impurities associated with commercial grades of aluminum. In those instances where relatively small amounts of iron and/or silicon may be prejudicial to the use of the resultant titanium product even higher purity aluminum (e.g., 99.75 percent or above) should be used.

In those embodiments of the invention wherein the aluminum is caused to react while in the solid state, the aluminum is preferably in finely-divided form. Suitable forms include chips, turnings, filings, or powders of essentially pure aluminum. In order to further facilitate the reaction, it is preferable to employ finely-divided aluminum which has been subjected to an activation procedure. Various procedures for suitably activating aluminum are known in the art and include procedures referred to in U.S. 2,885,314, Canadian 707,778, British 788,619, Canadian 673,753, and other available references. It will be evident, of course, that the activation procedure selected for use should not introduce, or result in the introduction, into the reaction system of this invention of significant quantities of ancillary materials prejudicial to the present process.

A feature of this invention is the fact that it can be carried out under widely differing temperature conditions and for varying periods of time. For example when the process is conducted in an organic reaction medium in which titanium tetrafluoride is soluble, temperatures as low as 115° C. have been found entirely operable. Accordingly when using such organic reaction media the reaction temperature will generally fall within the range of from about 100 to about 300° C. (or more) depending of course upon the identity of the particular organic diluent being used. When carrying the process out in the absence of an organic reaction medium it is generally preferable to employ temperatures ranging from about 200° C. up to about 2057° C., the boiling point of aluminum at atmospheric pressure. Suitable reaction times are of course dependent to some extent upon the particular process embodiment being practiced, the reaction temperature selected, the particular form in which the aluminum reductant is used and the like. Generally the reaction will proceed sufficiently rapidly as to be virtually complete in less than about four hours. In this connection, completion (or substantial completion) of the reaction is evidenced by the formation within the system of the metallic titanium product and accompanying formation of white crystals of aluminum fluoride.

In order to still further appreciate the practice and advantages of this invention, the following example is presented. It will be understood and appreciated however that this example is presented solely for the purpose of illustration and it is not to be construed as being limitative of this invention.

Example

In this experiment, finely-divided activated aluminum was caused to react with titanium tetrafluoride in refluxing anhydrous pyridine. More particularly, 3.6 grams of finely divided aluminum (previously activated by heating with a hydrocarbon solution of triethyl aluminum), 12.4 grams of titanium tetrafluoride and 80 milliliters of pyridine (previously dried and distilled under a nitrogen atmosphere) were placed in a 200 milliliter one-necked round bottom flask in a dry box containing a nitrogen atmosphere. The reaction flask was then removed from the dry box and attached to a reflux condenser. A small flow of anhydrous helium gas was maintained in the reaction system. As soon as the reactants were brought together in the reaction flask the solution turned light brown in color. As the contents of the flask were brought up to reflux temperature (approximately 115° C.) the solution became progressively darker. After one-half hour of refluxing a black ring had formed at the edge of the solution. Also small black particles (the titanium product) were observed in the system. The system was continuously refluxed for five hours. Thereupon the heating was stopped and the system allowed to stand for several days under a small pressure of the helium gas. It was then observed that the inside surface of the flask was coated with white solids, but the solution was still black or very dark brown. The contents were filtered under dry nitrogen atmosphere using a vacuum pump and the solid products (titanium and titanium-aluminum alloys admixed with aluminum fluoride) were maintained in suitable containers under a nitrogen atmosphere.

It will be readily apparent that various methods may be used for effecting separation between the metalllic titanium product(s) and the aluminum fluoride. One particularly efficacious method involves extracting the aluminum fluoride by means of a suitable inert solvent for the aluminum fluoride. For this purpose deaerated water (especially when heated) dissolves the aluminum fluoride without materially detracting from the usefulness of the titanium product. Other suitable solvents include low molecular weight alcohols, mutually soluble mixtures of alcohols and water, dimethyl sulfoxide, liquid hydrogen cyanide, or the like, especially where reactive gases (e.g., molecular oxygen, molecular nitrogen, etc., are excluded both from the solvent and the system). These extraction procedures should of course be conducted under a suitable inert or protective atmosphere so as to avoid oxidation or nitriding of the titanium product. The use of inert gases such as helium, neon, argon and the like are particularly useful as protective atmospheres.

It will be understood of course that the process of this invention may be carried out at reduced or elevated pressures although for most purposes it is preferable to conduct the reaction at atmospheric pressures.

Exemplary organic reaction media for use in accordance with certain embodiments of this invention include 2-allyl pyridine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-benzylpyridine, 3-benzylpyridine, lutidine, 2-ethyl pyridine, 3-ethyl pyridine, 4-ethyl pyridine, α-parvoline, β-parvoline, α-collidine, β-collidine, γ-collidine, piperidine, 2-isopropyl pyridine, 4-isopropyl pyridine, 4-methoxy pyridine, picoline, nicotyrine, 2-phenyl pyridine, 3-phenyl pyridine, 4-phenyl pyridine, conyrine, γ-coniceine, aldehydine, and the like.

What is claimed is:

1. A process for the concurrent production of aluminum fluoride and a metallic titanium product selected from the group consisting of titanium, aluminum-titanium alloys, and mixtures thereof which comprises reacting titanium tetrafluoride with metallic aluminum (a) in an essentially anhydrous organic reaction medium in which titanium tetrafluoride is soluble, said medium being further characterized in that at the reaction temperature being employed it is both chemically stable and in the liquid state; and (b) at a temperature sufficiently high and for a period of time sufficiently long to effect essentially complete chemical reduction of at least a portion of the titanium tetrafluoride.

2. The process of claim 1 wherein said reaction is conducted in refluxing pyridine.

3. The process of claim 1 wherein said aluminum is finely-divided, activated aluminum.

4. The process of claim 1 wherein (i) said reaction is conducted in refluxing pyridine and (ii) said aluminum is finely-divided, activated aluminum.

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