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PRODUCTION OF TITANIUM TETRACHLORIDE

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This invention relates to the manufacture of titanium tetrachloride and particularly to the manufacture of titanium tetrachloride from concentrates resulting from the smelting of ilmenite or other titanium-iron-oxide ores to remove the major part of the iron. These ores customarily contain oxides of calcium, magnesium, aluminum and silicon in substantial quantities and minute quantities of other metal oxides, in addition to oxides of titanium and iron.

The principal object of the invention is to provide an improved process suitable for treating iron-impoverished concentrates of these ores on a large scale to produce titanium tetrachloride of the required purity for use in the production of titanium metal.

Another object of the invention is to produce directly from such concentrates by means of a combination of chloridization, sublimation, and condensation operations, a titanium tetrachloride product containing, at most, only minute traces of iron.

A further object of the invention is to provide a process of the type mentioned which requires no elaborate, expensive, or difficult purification process to remove iron impurities from the product so produced.

Most of the efforts to produce titanium tetrachloride suitable for use in the production of titanium metal have been devoted to the treatment of natural titanium ores with various chloridizing agents to convert the iron and titanium oxides of the ores to ferric chloride and titanium tetrachloride, these chlorides being sublimed and separated in various ways. In some cases the iron and titanium chlorides have been formed and sublimed together and thereafter largely separated by fractional condensation. A partial separation of the iron and titanium chlorides in this manner is readily accomplished by reason of the fact that titanium tetrachloride condenses at a temperature several hundred degrees below the temperature at which ferric chloride condenses. However, a serious problem exists because the iron chloride tends to condense in an extremely finely divided form and to be entrained with and condensed with the titanium tetrachloride. This has required the employment of elaborate, expensive, and difficult purification operations for freeing the titanium tetrachloride of iron chloride. As a result, fractional condensation has been a most unsatisfactory procedure for separating any large quantity of iron chloride from titanium tetrachloride.

In other cases, efforts have been directed to selectively chloridizing and subliming the iron component of the ore so as to leave a substantially iron-free titanium oxide concentrate and thereafter chloridizing and subliming the titanium component of the residue to produce a substantially iron-free titanium tetrachloride. However, these efforts have met with indifferent success. Substantially complete removal of the iron in this manner has been accomplished only by chloridizing and subliming with the iron large amounts of titanium, which could not be readily recovered as an iron-free titanium tetrachloride. Anything less than substantially complete removal of the iron left a residue from which an iron-free titanium tetrachloride still could not be produced without employing the same objectionable purification operations which the art was seeking to avoid.

To the best of my knowledge, there has been no commercially practical process, prior to the present invention, for producing a substantially iron-free titanium tetrachloride by chloridizing a material containing compounds of titanium and iron together with compounds of calcium, magnesium, aluminum, silicon, etc., without the necessity for employing the objectionable purification operation referred to above to remove iron impurities from the product.

In accordance with U. S. Patent No. 2,476,453 to Peirce et al., ores composed largely of oxides of titanium and iron, such as ilmenite and the like, are smelted with little or no added flux in an electric arc furnace in the presence of coal as a reducing agent. The added flux is lime, and the amount used is limited to about 6 parts or less by weight per 100 parts of ore, depending upon the amount of lime, magnesia, and other fluxing agents naturally present in the ore. The amount of coal used ranges from about 8 to 14 parts by weight per 100 parts of ore, depending upon the amount of iron oxide in the ore, the amount of coal being somewhat less than would be required to reduce all of the iron oxide in the ore to metallic iron. When smelted at a temperature in the range of about 1500 to 1700° C. under the conditions described in the Peirce et al. patent, the charge separates into a molten iron of low titanium content and a highly fluid slag containing the bulk of the titanium and the added and naturally present fluxing agents. The molten iron and the fluid slag are separately tapped from the furnace, the iron being cast into pigs for general use in the iron and steel industry, and the slag, which still contains a substantial amount of iron but very little carbon, being used to some extent in the sulphuric acid digestion process for producing titanium dioxide pigment.

Whereas conventional prior smelting processes generally left the titanium of the ore largely in the form of a rutile type titanium dioxide that was substantially or largely insoluble in sulphuric acid and, therefore, not suitable for acid digestion, the process of the Peirce et al. patent leaves the titanium largely in the form of acid-soluble titanates. An approximate, typical analysis of such slags, which will vary considerably according to the ores from which they are produced and permissible variations in the smelting process, is as follows:

	Percent
TiO_2	70.4
Fe	8.0
C	0.12
CaO	1.10
MgO	5.20
Al_2O_3	6.30
SiO_2	6.10
Undetermined	2.78
	100.00

While Peirce et al. indicate that the iron in the slags produced in accordance with their patent is in the form of unreduced oxide, attempts to reduce the iron in the slag with hydrogen gas at 1000 to 1100° C. have produced substantially no loss in weight of the slag (which would result from the removal of oxygen from the iron oxide). This indicates that much of the iron content of the slags is in elemental form rather than in the form of oxide.

Huge quantities of titanium ores have been and are being smelted in accordance with the above-mentioned patent to Peirce et al. to produce pig iron and leave a titanium rich slag. Such slags form a readily available

and plentiful source of titanium for pigment manufacture and, potentially, for making titanium tetrachloride.

A further and more specific object of the present invention is to produce titanium tetrachloride from the slags resulting from the process disclosed in the above-mentioned patent to Peirce et al.

This application is a continuation-in-part of my copending application, Serial No. 352,826, filed May 4, 1953, now U. S. Patent 2,752,300, for Beneficiating Titanium Oxide Ores.

I have found that the process described and claimed in my said copending application is adaptable to the removal of residual iron from titanium slags produced in accordance with the above-mentioned patent to Peirce et al. The residual iron can be so completely removed from such slags by selective chloridization, in accordance with said copending application, that the resulting titanium concentrate can be directly chloridized to produce a titanium tetrachloride sublimate condensable to a substantially iron-free liquid requiring only a relatively simple final purification for use in the production of titanium metal. The condensed sublimate, without any purification, is a clear liquid ranging in color from a pale yellow or straw color to water white, and the iron content, which is responsible for any yellow color, ranges from around 0.1% down to 0.05% or less, depending upon the precision with which the process is controlled.

The first step in the process of my said copending application involves a preliminary carbon reduction of the iron oxide that is present in much larger amounts in ordinary titanium oxide ores, such as ilmenite. This preliminary reduction has the two-fold purpose of putting the ore into a more suitable physical form for handling in a chloridizing reactor and for putting the iron component of the ore into metallic form for more rapid and complete chloridization. However, I have found that titanium slags produced in accordance with the above-mentioned patent to Peirce et al. require no such preliminary reduction. This may be due in part to the fact that such slags are already quite porous due to the evolution of carbon monoxide during their formation in accordance with the patent to Peirce et al., in part to the low iron content of the slags, and possibly also in part to the fact that a large portion of the iron is already in metallic form, rather than in oxide form as indicated by Peirce et al.

Accordingly, in accordance with the present invention, the slag to be processed is heated to a temperature in the range of about 775 to 1100° C., preferably about 850 to 950° C., in a closed reactor having an inlet conduit for introducing a chloridizing gas and an outlet conduit for removing a sublimate. While the slag is held within such temperature range anhydrous hydrogen chloride is passed into the reactor and through the slag mass, in the substantial absence of air, to obtain intimate contact with the slag for reaction with the iron present therein. The hydrogen chloride is highly reactive with the iron under such conditions and is efficiently utilized to convert the iron to a ferrous chloride sublimate. Only about a 20 to 30% excess of hydrogen chloride is required to reduce the iron content of the slag to about 0.1%. Phosphorous pentoxide is also chloridized and sublimed, but the other constituents of the slag, in the substantial absence of carbon, remain unaffected in the residue, except to the extent that ferrous titanate is decomposed to leave the titanium component in the form of oxide, predominantly if not substantially entirely TiO_2.

The hydrogen chloride reaction is represented by one or both of the following formulae, depending upon whether the iron in the slag is in the form of metallic iron, ferrous oxide (including ferrous titanate), or both:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$

The substantial absence of water vapor in the sublimate tends to confirm my opinion that the iron in the slag is already at least largely in the form of metallic iron.

The sublimate is drawn off through the sublimate conduit as it is formed, and the ferrous chloride is preferably condensed at about 350 to 650° C. under anhydrous conditions and electrolyzed in a fused alkali metal chloride bath, as explained in my above-mentioned copending application, and as disclosed in greater detail in my copending application Serial No. 214,988, for Fused Bath Electrolysis of Metal Chlorides, filed March 10, 1951, now U. S. Patent 2,752,303. In such case the electrolysis of the ferrous chloride is carried out in a closed electrolytic cell while continuously passing dry hydrogen gas into the fused bath to react with chlorine released at the anode and regenerate anhydrous hydrogen chloride suitable for reuse in the first step of the slag treating process. Substantially pure iron powder suitable for many uses in the metallurgical arts is deposited on the cathode and the major portion of the hydrogen chloride entering the system in the first step of the process is recovered from the electrolytic cell as it accumulates. The remainder of the hydrogen chloride used in the first step of the process, along with any phosphorous chloride in the sublimate, passes through the ferrous chloride condenser, also taking with it any water vapor in the sublimate. This hydrogen chloride may be dehydrated, purified, and reused if desired.

The slag residue in the reactor is then thoroughly mixed with an amount of carbon calculated to form carbon monoxide with all of the oxygen combined with titanium in the residue (calculated as TiO_2). A second chloridizing reaction is then brought about in essentially the same manner as the first, but using dry chlorine as the reagent. A temperature in the range of about 775 to 1100° C. may be employed, but about 900 to 1000° C. is preferred to obtain a rapid reaction while avoiding the chloridization of anything but the titanium component of the residue. Under such reaction conditions, and in the presence of the amount of carbon specified, substantially all of the titanium may be rapidly converted to $TiCl_4$, which is drawn off as a gas as it forms and is condensed to a liquid.

So long as the amount of carbon does not exceed the amount required to take care of the oxygen combined with titanium, as explained above, the other components of the iron-depleted residue present in significant amounts (CaO, MgO, Al_2O_3, and SiO_2) again remain unaffected, except to the extent that such oxides combined with titanium as titanates are released as free oxides. Other metals present in the slags as oxides generally total around 1% or less of the original slag. To the extent that any of these other metals may be chloridized, their amounts in the condensed $TiCl_4$ are negligible and cause no objectionable contamination.

The gaseous $TiCl_4$ is condensed at a suitable temperature, preferably below 0° C., by cooling the condenser with a mixture of ice and salt, solid carbon dioxide, or the like. Alternatively, of course, mechanical refrigeration or any other suitable cooling system may be employed. However, before the sublimate is cooled in this manner, it is preferably passed at low velocity along an extended path through a suitably baffled heat exchanger to gradually reduce the temperature to a range of about 100 to 200° C. In this manner, any entrained solid matter from the reactor can be practically entirely precipitated, and such minute quantities of other chlorides as may have been formed and sublimed from the reactor can be largely condensed and precipitated in the heat exchanger without difficulty.

The condensed titanium tetrachloride, produced as described, is substantially iron-free, and, at most, requires only a relatively simple, final purification step to be suitable for direct reduction to titanium metal by present commercial methods. In view of the great difficulties heretofore encountered in producing such a product, as

explained above, the results of the combination of steps constituting the present invention represent a major contribution toward simplifying and reducing the cost of a presently critical, strategic metal.

To illustrate the practice of the invention, the following specific example is given, it being understood, however, that the invention is not limited to the particular operating conditions and slag compositions employed therein.

Example

The reactor was charged with a finely crushed titanium slag of the type described having a titanium oxide content of about 72% by weight (calculated as TiO_2), an iron content of about 8.9% by weight (calculated as Fe), and a carbon content of only about 0.12%. The charge was heated to about 900° C. and held at that temperature for about nine hours while passing a steady stream of anhydrous hydrogen chloride slowly through the charge. A ferrous chloride sublimate was drawn off as it formed. Analysis of the residue showed an iron content of about 0.12% and TiO_2 content of about 81%. The residue was then mixed with the stoichiometric amount of finely divided carbon required to convert the oxygen in the calculated TiO_2 to carbon monoxide. This mixture was heated in the reactor to about 900° C. for about four hours while passing a steady stream of anhydrous chlorine through the mixture. Titanium tetrachloride in gaseous form was drawn off as it formed and was condensed in a condenser cooled with ice and salt to a temperature substantially below 0° C. The condensed titanium tetrachloride was a clear, pale yellow or straw-colored liquid containing only traces of iron. The final residue in the reactor was a pure white material except for a few particles of unreacted carbon.

From the foregoing, it will be appreciated that the objects of the invention have been accomplished in a simple and practical manner readily adaptable to large scale commercial operations.

In the foregoing description of the invention, references are made to anhydrous hydrogen chloride and anhydrous chlorine. These gases containing less than 1% water by weight are required for satisfactory operation and a maximum amount of water of 0.1 or 0.2% or so is preferred. The presence of larger amounts of water slows down the chloridizing reaction and makes it more difficult to recover anhydrous products from the sublimates.

It will be appreciated by those skilled in the art that numerous operational variants of the invention can be practiced in following the process of the invention, and that the apparatus employed may take any of a variety of forms.

Having described my invention, I claim:

1. A process of producing titanium tetrachloride from titanium ores originally containing oxides of titanium, iron, and alkaline earth metals, but which have been smelted in the presence of carbon to remove the major portion of the iron while leaving a substantial portion thereof in the residue as metal and convert the major portion of the titanium in the residue to titanates, comprising contacting such residue with a chlorinating gas consisting essentially of substantially anhydrous hydrogen chloride at a temperature in the range of 775 to 1100° C. to convert the remaining iron to ferrous chloride and volatilize the same, removing the ferrous chloride vapor to leave a substantially iron-free residue, contacting said residue with chlorine gas at a temperature in the range of 800 to 1100° C. to convert the titanium in the residue to titanium tetrachloride vapor, and removing and condensing the titanium tetrachloride vapor.

2. A process of producing titanium tetrachloride from titanium ores originally containing oxides of titanium, iron, and alkaline earth metals, but which have been smelted in the presence of carbon to remove the major portion of the iron while leaving a substantial portion thereof in the residue as metal and convert the major portion of the titanium in the residue to titanates, comprising contacting such residue with a stream of chlorinating gas consisting essentially of anhydrous hydrogen chloride at a temperature in the range of about 775 to 1100° C. in the substantial absence of air until substantially all iron remaining in the residue has been converted to ferrous chloride and vaporized, removing the ferrous chloride vapor to leave a substantially iron-free concentrate of the titanium values, contacting said concentrate with a stream of chlorine gas in the presence of an amount of carbon sufficient to form carbon monoxide with all of the oxygen combined with titanium in said concentrate, calculated as TiO_2, until substantially all of said titanium has been converted to titanium tetrachloride vapor, and removing and condensing said titanium tetrachloride vapor.

3. A process of producing titanium tetrachloride from titanium ores originally containing oxides of titanium, iron, and alkaline earth metals, but which have been smelted in the presence of carbon to remove the major portion of the iron and produce a substantially carbon-free, titanium enriched residue with the major portion of the titanium in the form of titanates and a substantial amount of residual iron as metal, comprising contacting such residue with a stream of chlorinating gas consisting essentially of anhydrous hydrogen chloride at a temperature in the range of about 775 to 1100° C. in the substantial absence of air and carbon until substantially all iron remaining in the residue has been converted to ferrous chloride and vaporized, removing the ferrous chloride vapor to leave a substantially iron-free concentrate of the titanium values, contacting said concentrate with a stream of anhydrous chlorine gas at a temperature in the range of 800 to 1100° C. in the substantial absence of air and in the presence of an amount of carbon sufficient to form carbon monoxide with all of the oxygen combined with the titanium in said concentrate, calculated as TiO_2, until substantially all of said titanium has been converted to titanium tetrachloride vapor, and removing and condensing said titanium tetrachloride vapor.

4. A process of producing titanium tetrachloride from titanium ores originally containing oxides of titanium, iron, and alkaline earth metals, but which have been smelted in the presence of carbon to remove the major portion of the iron and produce a substantially carbon-free, titanium enriched residue with the major portion of the titanium in the form of titanates and a substantial amount of residual iron as metal, comprising contacting such residue with a stream of chlorinating gas consisting essentially of anhydrous hydrogen chloride at a temperature in the range of about 775 to 1100° C. in the substantial absence of air and carbon until substantially all iron in the mixture has been converted to ferrous chloride and vaporized, removing the ferrous chloride vapor to leave a substantially iron-free concentrate of the titanium values, contacting said concentrate with a stream of anhydrous chlorine gas at a temperature in the range of 900 to 1000° C. in the substantial absence of air and in the presence of an amount of carbon sufficient to form carbon monoxide with all of the oxygen combined with titanium in said concentrate, calculated as TiO_2, until substantially all of said titanium in said concentrate has been converted to titanium tetrachloride vapor, and removing and condensing said titanium tetrachloride vapor.

5. A process of producing titanium tetrachloride from titanium ores originally containing oxides of titanium, iron, and alkaline earth metals, but which have been smelted in the presence of carbon to remove the major portion of the iron and produce a substantially carbon-free, titanium enriched residue with the major portion of the titanium in the form of titanates and a substantial amount of residual iron as metal, comprising contacting

such residue with a stream of chlorinating gas consisting essentially of anhydrous hydrogen chloride at a temperature in the range of about 900 to 1000° C. in the substantial absence of air and carbon until substantially all iron in the mixture has been converted to ferrous chloride and vaporized, removing the ferrous chloride vapor to leave a substantially iron-free concentrate of the titanium values, contacting said concentrate with a stream of anhydrous chlorine gas at a temperature in the range of 900 to 1000° C. in the substantial absence of air and in the presence of an amount of carbon sufficient to form carbon monoxide will all of the oxygen combined with titanium in said concentrate, calculated as TiO_2, until substantially all of said titanium in said concentrate has been converted to titanium tetrachloride vapor, and removing and condensing said titanium tetrachloride vapor.

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