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PURIFICATION OF TITANIUM CARBIDE AND SIMILAR MATERIALS

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5 Claims. (Cl. 209—5)

This invention relates to the purification of titanium carbide and zirconium carbide, and other refractory carbon-containing compounds of titanium and zirconium, such as the carboxides and cyanonitrides. More particularly, it relates to the removal of free carbon from such compounds which contain free carbon as normally prepared.

Titanium carbide has been extensively used as an abrasive material, as an ingredient of hard alloys for cutting tools, and for other purposes. For many of these purposes a product as free as possible from uncombined carbon is desired. With this end in view, various methods of purification have been suggested and tried without much success. For example, it is well known that certain impurities can be removed from certain ores by froth flotation methods. Although titanium carbide is not an ore but a chemical product, the idea occurred that similar methods might be applicable to its purification. Tests soon demonstrated that these methods are completely ineffectual in removing free carbon from titanium carbide. Elutriation was also tried, with no success. A method that has been found to be partially effective is to form an aqueous suspension of the impure titanium carbide, with the addition of tannic acid as a deflocculating agent, allow to settle, and then pour off or decant the supernatant liquor. This process may be repeated a number of times. The difficulty with this method is that, while a substantial percentage of the carbon is removed with the decanted liquor, about 20% of the titanium carbide, present as fine particles, is also removed or lost. Obviously, therefore, this method is quite wasteful. Furthermore, considerable skill is necessary in determining the most favorable moment for decantation, as the settling of the deflocculated particles proceeds continuously, the titanium carbide settling first.

It is therefore an object of this invention to remove free carbon from titanium carbide and similar materials. It is another object to remove such free carbon with only a slight loss of titanium carbide. It is another object to remove such free carbon to a greater extent than hitherto possible, and with a minimum consumption of time and materials. Other objects will appear hereinafter.

These objects are accomplished by treating impure titanium carbide containing free carbon with an aqueous soap solution, preferably of such a concentration that the titanium carbide settles out to a relatively coherent mass, from which the supernatant liquor, containing free carbon, can be poured or drained off substantially completely. This process is also applicable to the removal of carbon from titanium carboxide, zirconium carboxide, titanium cyanonitride, and zirconium cyanonitride. In the practice of the present invention the soap solution performs two functions. First, it forms a stable suspension or emulsion with free carbon or graphite. Secondly, it assists the titanium carbide in settling to form a coherent cake, which will remain substantially intact even when the settling vessel is turned on its side. This of course is of tremendous advantage in removing the maximum amount of liquor from the cake, and in securing an extremely clean separation. Both these functions may be illustrated by treating 10 grams of finely-divided titanium carbide with 40 cc. of plain tap water, without any soap addition. With such a treatment, including stirring, settling and decanting, both the titanium carbide and free carbon settle out, leaving a clear colorless liquid above. When the vessel is tipped on its side, the titanium carbide and carbon flows out with the liquid.

The present method is entirely different from ordinary flotation methods of concentrating ores in several respects. First, such flotation methods are usually applied to ores containing, for example, only a few percent of valuable materials, the rest being gangue. Secondly, in such flotation methods the valuable materials are recovered in the froth which floats at the top of the mixture, while the valueless gangue ultimately sinks to the bottom. In the present method, on the other hand, the valuable materials remain at the bottom. Thirdly, such flotation methods ordinarily secure a froth, in which the recovered materials are concentrated, while in the present method a froth, if secured, is purely incidental, the separated materials being dispersed throughout the liquid medium. In the present method, in fact, as hereinafter pointed out, a froth is undesirable. Fourthly, the separation, in froth flotation methods, is normally between the froth at the top, and the liquid and gangue at the bottom, the liquid and gangue being discarded together. In the present method, the separation is between liquid (including froth, if any) and the settled cake at the bottom, the liquid and froth (if any) being discarded.

In accordance with the present invention, finely divided titanium carbide or other similar material is thoroughly agitated with a soap solution of a suitable concentration. The material be-

ing treated should be relatively finely-divided before the treatment is commenced, in order to insure the most rapid contact of the soap solution with the particles, and to assist in forming a coherent cake at the bottom of the settling vessel. Grinding to too fine a state of division is preferably avoided because of the expense involved, and because of the increased time necessary for settling. In practice, material which is ground sufficiently fine that 5% or less remains on a 325 mesh screen has been found satisfactory. Material passing a 200 mesh screen may also be used, but with material much coarser than this the process loses most of its efficiency and utility. Some of these materials, such as titanium carbide and titanium cyanonitride, are produced in massive lumps, which must be crushed before being ground. As most of these materials are quite hard, the grinding step usually introduces impurities from the grinding balls used. When iron grinding balls are used, the iron is removed by treating with hydrochloric acid, in well known fashion.

For successful results, the concentration of the soap solution is of primary importance. If the concentration of the soap solution is too great, the carbon may be removed satisfactorily, but there is also removed at the same time a considerable proportion of finely divided particles of titanium carbide. These are not allowed to settle because of the strong emulsifying action of the soap. If, on the other hand, the concentration of the soap solution is too small, the soap will not have sufficient emulsifying action to retain the free carbon in suspension, and the titanium carbide will not form a coherent cake. In practice, concentrations between 0.1% and 1.5% are used, with a preferred concentration of 0.25% or 0.5%. At 0.5% settling is not as rapid as at 0.25% but at 0.5% the separation of carbon is better than at 0.25%. The preferred concentration will depend somewhat upon the nature of the material being treated and the results desired. The concentration will also depend to some extent upon the hardness of the water being used and the strength or emulsifying power of the soap.

The absolute quantity of soap to be used, irrespective of the concentration employed, will depend upon the quantity of carbon to be removed (i. e. relative impurity of the starting materials), the hardness and amount of the water used, and the amount of titanium carbide being treated. In actual practice, it has been found that about 10 grams of soap per kilogram of material being treated produces satisfactory results. Of course it is understood that this quantity is merely illustrative and not limitative. This treatment may be repeated as many times as desired to reduce the free carbon content to the desired value. Thus, it is possible and usually desirable to employ a plurality of successive treatments instead of a single treatment. Such a procedure might be advantageous in treating large batches of material in a relatively small vessel. In addition, since the soap solution will be heavily laden with carbon, removal of such solution and substitution of a cleaner solution is desirable.

The titanium carbide and soap solution is agitated for a suitable period of time, sufficient to secure thorough emulsification of the carbon particles by the soap. The time required for agitation depends on the size of the batch, the quantity of carbon to be removed, and the fineness of subdivision of the starting material. There is no harm, except from an economical standpoint, in stirring or agitating for a prolonged period of time, and this is often desirable in order to insure that the maximum amount of carbon may be removed. In carrying out the agitation, it is preferred to keep the stirring mechanism as much as possible below the surface of the liquid, in order to avoid the formation of froth. If froth is present, it tends to stay in the mixing vessel and not to pour off with the decanted liquid. The result is that it is rendered more difficult to cleanly separate the coherent titanium carbide cake from the remainder of the mixture.

After the agitation is completed, the mixture is allowed to settle, preferably for a period of time sufficiently long that the titanium carbide settles to form a relatively coherent cake. At this point the liquid above the titanium carbide cake will be black in color, due to the suspended carbon contained therein. By "coherent cake" is meant a cake which does not disintegrate when the settling vessel is turned on its side to pour off the supernatant liquid. The cake is not so hard and coherent, however, that it cannot be stirred up again. The period of time for accomplishing this effect depends on several factors, these being: size of the batch being treated, fineness of subdivision of the starting material, and concentration of the soap solution used. The settling period can be as long as is desired, since there is no danger of the carbon settling out, as the emulsion is perfectly stable.

After the settling period has elapsed, the vessel is carefully turned on its side to pour off the supernatant liquor, and may be allowed to remain in that position until the liquor has thoroughly drained off from the titanium carbide cake. In practice, it is usually desired to turn the vessel back upright when the supernatant liquor has been completely removed, and the liquor draining off from the interior of the titanium carbide cake begins to carry with it excessive quantities of titanium carbide fines. The cake may then, if desired, be washed to remove as much of the residual soap and liquor as possible. The soap treatment may be repeated, if necessary, to remove additional carbon.

The invention having been described generally, the following specific examples are now given:

Example 1

100 grams of titanium carbide ground to −325 mesh and containing 1.79% of free graphite was added to 400 cc. of a .25% solution of flakes of a commercial sodium fatty acid soap, such as "Ivory" soap, in ordinary tap water, in a 500 cc. graduate, the mixture shaken well and allowed to settle. At the end of 5 hours, the titanium carbide had settled out, with a sharp separation between the titanium carbide and the liquor, to a cake coherent enough to decant the liquor by tipping the graduate on its side without disturbing the titanium carbide cake. The cake was then dried. This treatment reduced the free graphite content to 1.07%. The recovery was 89.5%.

Example 2

2000 grams of finely-divided titanium carbide (secured from the decantations or waste material resulting from purification of titanium carbide with tannic acid) containing 5.73% free graphite was added to 2750 cc. of an aqueous solution containing 8.25 grams of flakes of a commercial sodium fatty acid soap, such as

"Ivory" soap, in a 4 liter beaker. The mixture was stirred for 15 minutes, and then allowed to settle for 3 hours. At the end of this time most of the titanium carbide had settled to a coherent cake. An intermediate layer, containing free graphite and some titanium carbide, and an upper layer containing free graphite, were decanted or poured off and discarded by turning the beaker on its side. A solution containing 10 grams of flakes of a commercial sodium fatty acid soap, such as "Ivory" soap, in 2300 cc. of water was then added to the cake, and stirred, settled and decanted as before. The second cake was then treated with 2300 cc. of an aqueous solution containing 10 grams of "Ivory" soap flakes, stirred and settled as before. The liquor only formed a single layer with this treatment, the titanium carbide settling to form a coherent cake. The liquor was decanted by turning the vessel on its side, and the cake was then dried. 1772 grams of titanium carbide containing only 0.74% free graphite were recovered.

Example 3

227 pounds of titanium carbide containing small amounts of combined oxygen (as titanium carboxide) and over 1% free graphite was wet milled to −325 mesh. The milled slurry was placed in a 55 gallon rubber lined tank and enough water added to give a total volume of about 50 gallons. 908 grams of flakes of a commercial sodium fatty acid soap, such as "Ivory" soap, were added, and the mixture stirred for 1 hour. It was then allowed to settle for 20 hours. The tank was then tipped on its side, decanting off the liquor (containing the free graphite) without disturbing the coherent titanium carbide cake formed at the bottom. The cake was then given a second treatment with the same amount of water and soap, and stirred, settled and decanted as before. The dried cake showed only 0.22% free carbon. The recovery was 82.8%.

Example 4

20 grams of zirconium carbide, or of zirconium cyanonitride, or of titanium cyanonitride was shaken with 20 cc. of water and 10 cc. of a 1% solution of a commercial sodium fatty acid soap, such as "Ivory" soap, in a test tube. The zirconium carbide, or zirconium cyanonitride, or titanium cyanonitride settled out to a coherent cake. The free graphite remaining in the upper layer was poured off by turning the test tube on its side. After washing, the particles had a bright metallic luster.

Besides the "Ivory" soap, which is a commercial sodium fatty acid soap, mentioned in the above examples, other water-soluble sodium and potassium soaps may be used, such as "Fels-Naphtha" soap, which is a commercial sodium fatty acid soap, liquid soaps, etc. Other modifications may obviously be made within the scope of the invention, and it is not intended to be limited except as defined by the appended claims.

I claim:

1. A method of removing free carbon from a material taken from the class consisting of the carbides, cyanonitrides and carboxides of titanium and zirconium, comprising agitating said material with a soap solution having a concentration between 0.1% and 1.5%, allowing to settle, and pouring off the supernatant liquor.

2. A method of removing free carbon from a material taken from the class consisting of the carbides, cyanonitrides and carboxides of titanium and zirconium, comprising agitating said material with a soap solution having a concentration between 0.1% and 1.5%, allowing to settle until said material forms a coherent cake, and draining off the supernatant liquor.

3. A method of removing free carbon from titanium carbide comprising agitating said titanium carbide with a soap solution having a concentration between 0.1% and 1.5%, allowing to settle, and pouring off the supernatant liquor.

4. A method of removing free carbon from titanium carbide comprising agitating said titanium carbide with a soap solution having a concentration between 0.1% and 1.5%, allowing to settle until said titanium carbide forms a coherent cake, and draining off the supernatant liquor.

5. A method of removing free carbon from titanium carbide comprising agitating said titanium carbide with a soap solution having a concentration between 0.25% and 0.5%, allowing to settle until said titanium carbide forms a coherent cake, and draining off the supernatant liquor.

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