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FLEXIBLE FELTABLE FIBERS OF TITANIUM NITRIDE AND THEIR PREPARATION

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This invention relates to new inorganic fibrous materials and to their preparation. More particularly this invention relates to a novel fibrous form of titanium nitride and to a process for its preparation.

Titanium ntiride has been known for a long time and has been the subject of much investigation. It is generally bronze yellow in color and is resistant to attack by inorganic acids. It is particularly resistant to high temperature, having a melting point reported to be over 2900° C. The nitride has a high electrical conductivity.

Titanium nitride has been obtained by the reaction of a titanium halide and nitrogen or of titanium oxide with a reducing agent and nitrogen. The processes heretofore employed have given titanium nitride in a finely divided state or as a layer. Bars of sintered titanium nitride are reported to be brittle (Schwarzkopf and Kieffer, "Refractory Hard Metals," Macmillan, N.Y., 1953, page 233). This suggests a low tensile strength for the material. No fibrous form of titanium nitride has been reported and particularly none which is highly flexible.

It is an object of this invention to provide new inorganic fibrous materials and a process for their preparation. A further object is to provide a novel fibrous form of titanium nitride and a process for its preparation. Another object is to provide a fibrous form of titanium nitride which is highly flexible. Still another object is to provide titanium nitride in the form of asbestos-like fibers having high tensile strength and outstanding flexibility. Other objects will appear hereinafter.

These and other objects are accomplished by the following invention which comprises an inorganic asbestos-like flexible fiber consisting essentially of titanium nitride and characterized in that said fiber has a diameter of less than about 10 microns and a flexibility sufficient to permit bending around a mandrel of 1 mm. diameter without breaking. There have now been prepared as new inorganic fibrous materials, the asbestos-like form of titanium nitride characterized in that it is in the form of flexible fibers each having a diameter of less than about 10 microns with a length of at least 10 times the diameter and a flexibility sufficient to permit wrapping around a mandrel of 1 mm. diameter without breaking.

The fibrous product consisting predominantly of titanium nitride is obtained by passing a mixture of titanium tetrachloride and nitrogen in a slowly moving stream of not more than 300 linear cm./hour measured under standard conditions of temperature and pressure into contact with a siliceous material heated to a temperature of at least 1225° C. and in the presence of a reducing agent, and removing the fibers that are formed.

The following examples illustrate the preparation and properties of the new fibers.

Example I

Pelleted channel black carbon (5.4 parts by weight) having a specific surface area of 625 sq. meters/g. was placed in a mullite-bonded ($Al_6Si_2O_{13}$) alumina ceramic boat which, in turn, was placed in a mullite ceramic tube. Nitrogen flowing at a rate of approximately 0.05 mole/hr. was dried to a dewpoint of about −80° C. by passage through a solid CO_2 cooled vessel and then bubbled through titanium tetrachloride which vaporized

at a rate of 0.00044 mole/hr. This gas mixture was slowly passed through the tube during heating for 4.5 hours at 1425–1450° C. After cooling of the product under nitrogen flow, it was found that the surface of the carbon was covered with burnished gold-colored fibers having a wide range of diameters from less than 1 micron to several microns and up to about 1 cm. in length. The fibers were flexible and could be bent sharply without breakage. The X-ray diffraction pattern of the fibers indicated they were of titanium nitride. During this reaction, the boat (originally 12.8 parts) lost 1.5 parts and the contents showed a net loss of 0.8 part. Other products either in the boat or deposited downstream therefrom were colorless fibers which gave an X-ray diffraction pattern corresponding to beta-silicon carbide and silica.

Repetition of the above general procedure with 2.182 g. of carbon, 1.7 g. titanium tetrachloride for 5 hours at 1440–1450° C. gave fibrous titanium nitride and fibrous rutile.

When the above general procedure was repeated except that a temperature of 1300° C. was used, fine fibers were likewise obtained.

Example II

An alumina boat containing 0.85 g. of carbon black ("Neospectra') was heated in a mullite (aluminum silicate) tube (1¼" internal diameter x 30" long) to 1435 to 1450° C. in a stream of nitrogen. The nitrogen stream flowing at a rate of 0.079 mole/hr. was bubbled through heated titanium tetrachloride which vaporized at a rate of 0.003 mole/hr. The titanium tetrachloride vapors in nitrogen were then conducted through the mullite tube over the heated carbon black. After 6 hours, the titanium tetrachloride flow was stopped and the boat and its contents were allowed to cool to room temperature under nitrogen. The contents of the boat at the end weighed 0.94 g. and gave an X-ray pattern corresponding to that of titanium nitride. The boat decreased in weight from 14.96 g. at the start of the experiment to 13.75 g. at the end. On the sides and surfaces of the boat was a growth of bronze-colored fibers (0.04 g.) that gave an X-ray diffraction pattern for titanium nitride. These fibers were found to contain 15.94–14.78% N (two determinations). The fiber diameter was 0.05 to 1.0 micron and the length was up to 5 mm.

Example III

A graphite boat containing 0.99 g. of powdered alumina covered with a layer of carbon black weighing 0.49 g. was heated in a mullite tube (1¼" internal diameter x 30" long) in a stream of nitrogen to 1395–1450° C. Titanium tetrachloride (0.00069 mole/hr.) and nitrogen at 0.050 mole/hr. were passed over the hot charge for 6–8 hours. At the end of the experiment the tube was found to contain a downstream fiber plug (0.15 g.) that gave an X-ray diffraction pattern corresponding to beta-SiC (cubic) and face centered cubic crystals of cell constant a_0 4.26 A. (TiO and TiN have a_0 4.235 A.; TiC has a_0 4.32 A.). A deposit of brown to gray fibers above the boat at the upstream end weighed 0.09 g. and contained individual fibers as long as 1.0 cm. with a diameter of 0.06–3.0 microns. These fibers gave an X-ray diffraction pattern indexed as face-centered cubic, a_0 4.26 A., indicative of a TiN fiber containing dissolved TiO and TiC.

Example IV

An alumina boat containing 5.64 g. of 20–30 mesh aluminum metal powder was heated in a 1¼" internal diameter mullite tube in a stream of N_2 to 1385–1475° C. Nitrogen (0.06 mole/hr.) and $TiCl_4$ vapor (0.0014 mole/hr.) were passed over the hot charge for 7 hours. After allowing the tube and its contents to cool to room temperature under nitrogen, it was found that golden fibers had deposited on the tube walls above the boat (0.14 g.). The X-ray diffraction patterns of these fibers corresponded to TiN probably containing some Al_2SiO_5. The fiber diameter was 0.58 to 2.0 microns and the length ranged to over 1.0 cm.

Example V

Example IV was repeated except that commercial aluminum sheet (6.65 g.) was used in place of the powder and this was heated to 1350–1450° C. in argon instead of nitrogen. After reaction temperature was reached, argon at 0.012 mole/hr., nitrogen at 0.025 mole/hr. and titanium tetrachloride vapor at 0.00044 mole/hr. were passed over the hot charge. The boat and the upstream surface of the aluminum residue were covered with beautiful long golden fibers. Some individual fibers over 1 cm. long were observed. The golden fibers (0.025 g.) gave an X-ray diffraction pattern for titanium nitride face-centered cubic crystals, $a_0=4.25$ A. The X-ray pattern of the golden fibers was not changed by treatment with 48% hydrofluoric acid. In addition to the golden fibers, 0.15 g. of gray fibers was formed upstream (X-ray pattern: face-centered cubic cell, a_o 4.25 A.). The fiber diameter was 0.10 to 3.0 microns.

Example VI

Example V was repeated except that $TiCl_4$ vapors (0.0029 mole/hr.) and argon (0.050 mole/hr.) were first passed over hot titanium sponge (to give $TiCl_3$ and $TiCl_2$) before mixing with nitrogen and passing over the aluminm charge. Golden fibers of TiN formed on upstream surfaces of boat. White and gray fibers having the X-ray pattern of aluminum nitride formed on downstream surfaces of boat and its contents.

Example VII

Magnesium turnings (3.58 g.) were heated in an alumina boat in 1¼" I.D. mullite tube in nitrogen to 1340–1450° C. Nitrogen (0.37 mole /hr.) and $TiCl_4$ vapor (0.0016 mole/hr.) were passed over the hot charge for 5 hours. After allowing the tube to cool under nitrogen to room temperature, it was found that 0.03 g. of long (up to 1.0 cm.) golden fibers had deposited on the upstream end of boat. The X-ray diffraction pattern of the fibers was identical with that of TiN. The fiber diameter was 0.12–3.0 microns.

Example VIII

Calcium nitride (Ca_3N_2, 7.43 g.) was heated in an Alundum boat in a 1¼" I.D. mullite tube in N_2 to 1245–1425° C. Nitrogen (0.028 mole/hr.) and $TiCl_4$ vapor (0.0013 mole/hr.) were passed over the heated charge for 4 hours. A deposit of 0.19 g. of gray-brown fibers giving the X-ray diffraction pattern of TiN was removed from the upstream end of the boat and the adjacent walls of the mullite tube. This fiber diameter is 0.04–4.0 microns with a length of up to 8 mm.

Example IX

A mullite tube (1¼" I.D. x 30" long) was heated to 1330–1425° C. at its mid-section. Titanium tetrachloride (0.0025 mole/hr.) and hydrogen (0.020 mole/hr.) were introduced to the hot zone through a vitreous silica tube from the left end of the mullite tube and ammonia (0.015 mole/hr.) was introduced through a similar tube from the right. Gaseous products were exhausted from the right end of the mullite tube. The flow of gases was maintained for 6.17 hours. A black and gray scale (0.11 g.) was recovered from the tube along with 10 mg. of long golden fibers of TiN (over 1 cm. long). One of these fibers was found to be hexagonal in cross section (11.6μ across corners of the hexagon) and was demonstrated to be capable of supporting a 50 g. weight without breaking. This is equivalent to a tensile strength for the fiber in excess of 1,000,000 lb./in.². A fiber 10 microns in diameter when bent to a 0.5 mm. radius of curvature, showed complete and almost instantaneous recovery without fracture of permanent deformation even after maintaining it as a coil for some time. Such recovery effects have not been found in single crystal metal fibers of comparable dimension. The electrical resistivity was 20 microohms-cm.

Example X

Example IX was repeated with the following conditions:

	Mole/hr.
$TiCl_4$	0.0140
NH_3	0.105
H_2	0.080

Temp., 1370–1470° C.
Duration of run, 3.25 hours.

A doughnut-shaped deposit (1.01 g.) of crude golden TiN fibers formed near the hottest zone of the mullite tube.

Analysis: Found—N, 13.06; Ti, 50.53, 51.35; Si, 7.13%.

Example XI

Titanium tetrachloride (0.0019 mole/hr.) and argon (0.035 mole/hr.) were passed over hot titanium sponge packed in a quartz tube and introduced through this tube to the hot zone of a surrounding mullite tube (1¼" I.D.) at 1230–1310° C. Ammonia (0.015 mole/hr.) was introduced into the mullite tube around the quartz tube. Golden fibers (1.01 g.) formed near the tip of the quartz tube. The X-ray diffraction pattern of these fibers indicated TiN plus a trace of α-quartz. Treatment of a 1.0 g. sample of these fibers with 48% HF and a small amount of H_2O_2 left a solid residue of 0.51 g. of golden fibers. The X-ray diffraction pattern of these golden fibers gave a face-centered cubic cell constant of a_o 4.235 A. The extracted fibers contained 16.79% nitrogen and 77.21% titanium. The fiber diameter was 0.5–6.0 microns.

Example XII

An alumina boat containing 2.36 g. of TiO was heated in a stream of N_2 in a 1¼" I.D. mullite tube to a maximum temperature of 1420° C. $TiCl_4$ (0.0023 mole/hr.) and N_2 (0.045 mole/hr.) were passed over the hot TiO for 6.58 hours. At the end of the experiment the surface of the TiO particles in the boat was covered with needles and fibers of TiN growing outward from the surface.

This invention provides a new form of titanium nitride, namely, a fibrous titanium nitride having high tensile strength and a high degree of flexibility. The fibers have a diameter of up to about 10 microns and are usually between 0.05 and 5 microns. The length of the individual fibers is at least 10 times their diameter and generally 100–1000 times the diameter. The flexibility exhibited by the fibers is outstanding. As shown in Example IX, a relatively thick fiber could be bent quite sharply and make complete recovery.

In addition to these outstanding properties, the titanium nitride fibers generally have an attractive color.

The fibrous form of titanium nitride is obtained by passing a mixture of titanium tetrachloride with nitrogen in the presence of a reducing agent at a temperature of at least 1225° C. and preferably over 1300° C. in the presence of siliceous material. The mixture is readily obtained by passing nitrogen through titanium tetrachloride prior to introduction in the hot furnace.

The titanium tetrachloride is a readily available volatile material. Nitrogen can be employed as gaseous nitrogen. In addition to nitrogen itself, ammonia can be used to react with titanium tetrachloride to give titanium nitride. The reducing agent can be solid or gaseous, i.e. a reducing atmosphere. Suitable reducing agents are elements such as hydrogen, carbon, aluminum, magnesium, calcium, titanium, iron, silicon, sodium, etc. Lower valent oxides, e.g., TiO, SiO, Al_2O, etc., or lower valent halides such as $SiCl_2$, $TiCl_2$ and $TiCl_3$ can also be used. Other reducing agents include metal nitrides such as aluminum nitride and magnesium nitride, metal hydrides such as calcium hydride, lithium aluminum hydride and titanium hydride as well as carbides such as silicon carbide. It is preferred that the reducing agent gives by-products which are volatile under the reaction conditions. The particularly useful reducing agents are aluminum, magnesium, calcium for their nitrides), carbon and ammonia. In the siliceous ceramic reactors employed, these reducing compounds are capable of producing SiO under the reaction conditions. The latter compound is an effective and important intermediate for the production of titanium nitride fibers.

The fibrous titanium nitride is formed when the titanium tetrachloride and nitrogen are passed slowly over a reducing agent or admixed in a reducing atmosphere in the presence of a siliceous material heated to a temperature of at least 1225° C. Rapid rates of gas flow inhibit fiber formation and the linear velocity of gaseous material should not exceed 300 linear cm./hour when measured as an input at standard temperature and pressure.

The temperature of the reaction vessel should be at least 1225° C. The maximum temperature depends upon the highest that the equipment will maintain without failure. Temperatures employed usually are not much in excess of 1500° C. and preferably 1300–1500° C.

In general the container employed in heating the reactants is a ceramic and generally a siliceous refractory. Fiber formation takes place in the presence of a silicon-containing material. Small amounts of a fibrous form of an inorganic silicon compound are generally present with the fibrous titanium nitride. However, the fibrous product is composed of titanium nitride in major amounts.

The fibrous product is removed by mechanical means from the refractory. Any fibrous inorganic silica compounds can be removed from the fibrous nitride by treatment with hydrogen fluoride.

Identification of the fibrous titanium nitride is accomplished by X-ray diffraction pattern data.

The new titanium nitride fibers have extremely good thermal stability, inertness and strength. Mats or felts of the fibers are readily obtained by suspending the fibers in a viscous liquid such as glycerine followed by filtration to remove the dispersing liquid. The mats are useful as filters, e.g., in air to remove solids or to remove bacteria from solutions. They are good thermal insulators, especially where extremely high temperatures are involved. The fibers can be incorporated in plastics to give increased stiffness and tear strength. They are reinforcing agents for fibers or papers. Finely ground fibers of titanium nitride when incorporated with oils such as silicone oil produce thick greases useful as lubricants.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An inorganic asbestos-like flexible feltable fiber consisting essentially of titanium nitride and characterized in that said fiber has a diameter of less than about 10 microns and a flexibility sufficient to permit bending around a mandrel of 1 mm. diameter without breaking.

2. An inorganic asbestos-like flexible feltable fiber of high tensile strength consisting essentially of titanium nitride and characterized in that said fiber has a diameter of between 0.05 and 5 microns with a length of at least 100 times its diameter and a flexibility sufficient to permit bending around a mandrel of 1 mm. diameter without breaking.

3. As a new inorganic fibrous material, the asbestos-like form of titanium nitride characterized in that it is in the form of flexible feltable fibers each having a diameter of less than about 10 microns with a length of at least 10 times its diameter and a flexibility sufficient to permit bending around a mandrel of 1 mm. without breaking.

4. As a new inorganic fibrous material, the asbestos-like form of titanium nitride characterized in that it is in the form of flexible feltable fibers of high tensile strength each having a diameter of between 0.05 and 5 microns with a length of at least 100 times its diameter and a flexibility sufficient to permit bending around a mandrel of 1 mm. diameter without breaking.

5. Process of preparing asbestos-like flexible feltable fibers consisting predominantly of titanium nitride which comprises passing and reacting titanium tetrachloride and nitrogen in a slowly moving stream having a linear velocity of not more than 300 linear cm./hour, measured under standard conditions of temperature and pressure, in contact with a siliceous material heated to a temperature of at least 1225° C. and in the presence of a reducing agent, and removing the asbesos-like flexible feltable fibers thus formed consisting predominantly of titanium nitride.

6. Process of preparing asbestos-like flexible feltable fibers consisting predominantly of titanium nitride which comprises passing and reacting titanium tetrachloride and nitrogen in a slowly moving stream having a linear velocity of not more than 300 linear cm./hour, measured under standard conditions of temperature and pressure, in contact with aluminum silicate heated to a temperature of 1300 to 1500° C. and in the presence of carbon, and removing the abestos-like flexible feltable fibers thus formed consisting predominantly of titanium nitride.

7. A composition of matter comprising a mat of titanium nitride flexible feltable fibers each having a diameter of less than about 10 microns with a length of at least 10 times its diameter and a flexibility sufficient to permit bending around a mandrel of 1 mm. diameter without breaking.

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