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SPINNABLE MULLITE FIBERS AND THEIR PREPARATION

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FIG. II

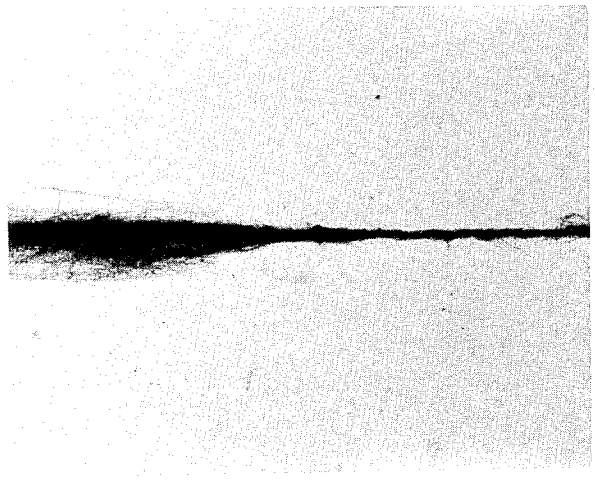
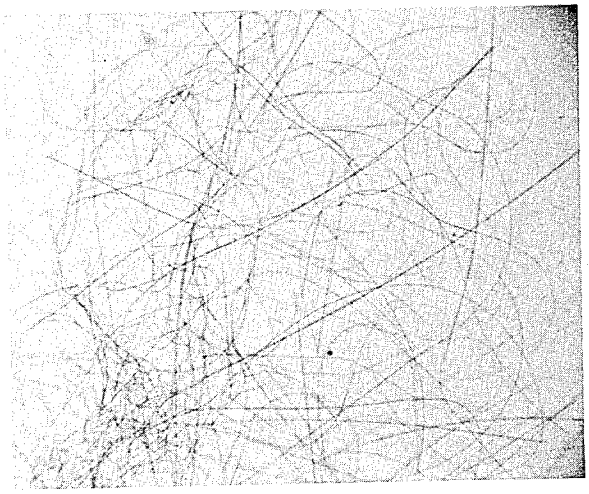


FIG. I



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SPINNABLE MULLITE FIBERS AND THEIR PREPARATION

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This invention relates to inorganic fibrous materials and their preparation. More particularly, this invention relates to novel mullite fibers which are spinnable and to a method for their preparation.

Fibrous forms of inorganic materials, both natural and synthetic, have been described. These include asbestos, potassium titanate, corundum, titanium dioxide, which may be described as staple fiber materials as well as the various types of glass fiber which exemplify continuous filament fiber materials. Although the synthetic inorganic staple fibers so far produced have been capable of forming felted or matted structures, it has not thus far been possible by synthetic means to produce a crystalline inorganic fiber capable of being spun in the sense that it can be picked, drafted and twisted to form threads and yarns.

It is an object of this invention to provide a new inorganic fibrous material and a method for its preparation. A further object is to provide novel mullite fibers which are spinnable and a method for their preparation. Other objects will appear hereinafter.

The present invention provides such synthetic fibers in the form of fibrous crystals of the aluminum silicate, mullite, sufficiently flexible to be spun.

The spinnable fibrous mullite crystals of this invention have a fiber cross-sectional dimension of less than 5 microns and an axial ratio, i.e., the ratio of length to cross-sectional dimension of at least 100:1. It is preferred that the cross-sectional dimension of the fibers be about 1 micron or smaller and that the axial ratio be at least 1000:1 since such fibers produce the strongest threads and yarns. For the most part, the fibers range up to 1–2 cm. in length and readily form matted or felted structures. The individual fibers are relatively free of overgrowths, dendrites and obvious twinning.

The flexibility of the fibers is illustrated in FIGURE I, while the fibers' ability to form a staple yarn is illustrated in FIGURE II. The figures are more fully discussed subsequently.

By virtue of their high form anisotropy, flexibility, toughness and intercrystal cohesion, masses of these fibers can be picked, drafted and twisted into a staple yarn. Because of their chemical resistance and highly refractory nature, these yarns as well as mats, felts, and the like, prepared from the mullite fibers of this invention, possess outstanding utility as thermal insulation and such structures constitute a part of this invention.

The mullite fibers of this invention are prepared by crystallization from a vapor phase derived by heating a mixture containing sources of silicon, oxygen, aluminum, and sulfur in an atmosphere containing at least 1% hydrogen at a temperature in the range of 800–1200° C. It is preferred that the reaction be carried out at temperatures in the range of 900–1100° C.

A suitable mixture for supplying the vapor phase required for formation of fibrous mullite consists of silica, aluminum and aluminum sulfide. The constituents of this mixture are preferably present in the proportions by weight of 2:1:1 (SiO_2:Al:Al_2S_3). It will be appreciated that mixtures of other compounds which yield these constituents under the conditions of fiber synthesis can be employed in lieu of the constituents themselves. For example, any sulfur compound which on reaction with

Al yields Al_2S_3 can be employed in place of Al_2S_3 itself. To insure homogeneity and intimate contact among the components, the mixture is intensively milled prior to use.

It is believed that the presence of small amounts of a fluoride in the mixture supplying the vapor phase is beneficial although the exact role of such fluoride is not understood. Very small proportions, i.e., as little as 0.01%, of a fluoride such as cryolite or aluminum fluoride appear to be effective.

The process of this invention is conveniently carried out by placing the reactants in a suitable container in a silica reaction tube. A mixture of an inert gas, for example, argon (95–99%) and hydrogen (1–5%) is contained in the tube and surrounds the reactants. The tube and contents are heated to a temperature of 800–1200° C. whereupon the mullite fibers form on the top edges and walls of the container and on the wall of the reaction tube above and isolated from the reaction mixture.

The reaction time is not a critical variable in the production of these mullite fibers and the process may be carried out during times ranging from a few minutes, i.e., 5–30 minutes to several days. When long reaction periods are employed, it may be necessary to remove accumulated mullite fibers from time to time.

This process is usually carried out at atmospheric pressure and the provision of equipment capable of withstanding pressures greatly in excess of atmospheric pressure is unnecessary. It may be desirable in certain cases to employ pressures slightly above atmospheric pressure to prevent access of atmospheric constituents or for other reasons. It is also possible to operate the process at reduced pressure. When such higher or lower pressures are employed, they will normally be within the range of 0.5–5 atmospheres.

After the desired reaction period, the reaction tube is cooled and the fibrous mullite is detached from the walls, e.g., by scraping. These fibers are generally obtained in a very pure condition and require no purification. However, any non-fibrous material present may be readily removed by suspending the product in water and allowing the suspension to settle. The fibrous product may then be recovered by any convenient means such as filtration, decantation and the like. Mats or felts of fibrous mullite are produced from such suspensions by filtration.

The most coherent and flexible felted mats are produced by filtration of suspensions of the finest fibers having the greatest ratios of axial dimensions. Thus, when dilute, i.e., less than 1%, suspensions are agitated vigorously, and then allowed to stand any adventitious large crystals having a non-fibrous habit or aggregates thereof quickly settle out and the more desirable materials still in suspension can be decanted therefrom. When the decanted suspension is again allowed to stand, the most fibrous material flocculates and entangles under the influence of gravity and the gentle agitation of natural convention currents. This flocculation can result in accelerated sedimentation of this preferred product which can then be isolated by decanting the suspending phase which now contains any fine powder inadvertently produced.

The properties of mats produced by filtration can be varied considerably in the sedimentation process by the relative amounts of fibrous mullite and non-fibrous by-products permitted to remain with the fibers. Stiffer mat structures are obtained by retention of coarser particles while fine particles may be retained in the fiber mat to alter density, porosity and other properties. Thus, fibrous mullite can be used as a binder for other materials, e.g., fillers and extenders such as silica, carbon, asbestos, titanium dioxide, potassium titanate, and the like, which can be introduced to provide additional desirable properties. The bulk density and other properties of felted mats can also be varied widely by suitable choice of fiber

and suspension characteristics, and by the conditions, e.g., pressure and temperature under which the suspending medium is separated from the fibers.

Although water is the most useful and practical dispersing and suspending medium, other liquids, e.g., alcohols, hydrocarbons, and the like, can be used. The properties of such suspensions and mats prepared therefrom can be modified by the addition of dispersing agents, other fibers, both natural and synthetic, organic and inorganic, and binders such as organic resins, sodium silicate, glass-forming materials, colloidal alumina or silica, to obtain properties desired for specific applications.

The mullite fibers of this invention can also be separated from non-fibrous contaminants by carding or combing. These methods are especially indicated when the mullite fibers are to be formed into a sliver, drafted and twisted to form yarns and threads. Properties of mullite yarns and threads can be advantageously modified by incorporating other fibers such as glass, asbestos, cotton, nylon, etc. and by applying yarn finishes such as solutions or dispersions of resins and fusible inorganic substances. Such yarns and threads are particularly useful as thermal insulation for wires, tubing, pipes, conduits, and the like, and in the construction of refractory fabrics. the yarns, threads and fabrics also find use in the reinforcement of plastic materials and as electrical insulation, particularly in applications necessitating exposure to high temperature.

The individual fibers of this invention are colorless but when matted together or spun into thread, they appear white. X-ray diffraction analysis of the fibers indicates that they have the mullite crystal structure. Microscopic examination indicates that most of the fibers have a ribbon-like form and for such fibers the ratio of the longest dimension to the intermediate dimension is referred to as the axial ratio. The ratio of the intermediate dimension, i.e., the width of the ribbon to the shortest dimension, is usually less than 10:1. These flat ribbons are readily spun to threads and yarns of good tenacity and are a preferred class of the spinnable mullite fibers of this invention.

The invention is illustrated by the following examples in which parts by weight are employed. The materials are of ordinary commercial purity.

EXAMPLE I

Two alumina boats containing 3.45 g. and 3.88 g., respectively, of a mixture of fine silica and aluminum dust (weight ratio 2:1), produced by ball-milling for 3 days with an equal volume of 8 mm. glass balls, were placed end to end in a large, horizontally positioned silica combustion tube having one end sealed shut. The silica employed in this example was prepared from sodium silicate by precipitation with sulfuric acid and contained sodium sulfate impurity. This impurity reacted with Al under the conditions employed for preparation of fibrous mullite to form Al_2S_3. The tube was attached to a vacuum system, evacuated, and heated. When a temperature of 700° C. had been attained, the tube was filled with argon and heating continued to a temperature of 1000° C. The tube and contents were heated for 100 hours at 1000–1035° C. and thereupon allowed to cool to room temperature. Upon removal of the boats, it was found that each had undergone a small weight loss (11 mg. and 27 mg., respectively) and that a growth of fine, colorless fibers had formed on the outer end of the boat nearer the end of the combustion tube connected to the vacuum system and in the tube surrounding this location. This fiber growth was in two bands. The fibers of the outer band were composed of silica as indicated by the fact that when the fibers were dissolved in 48% hydrogen fluoride a solution was obtained which left no residue on evaporation. The mullite fibers in the second band comprised fine, smooth curving ribbons considerably less than 1 micron in thickness, up to about 4 microns in width, and up to more than 1 cm. in length.

EXAMPLE II

A milled mixture of 1.7 g. of fine silica, 0.8 g. of aluminum dust and 0.5 g. of aluminum sulfide powder (Al_2S_3) contained in an alumina boat was placed in a vitreous silica test tube together with a similar boat containing 20 g. of a mixture of aluminum and iron powders (3:1 atomic ratio). The silica tube was placed in a silica jacket which was evacuated and heated to 880° C. At this temperature argon was admitted and heating continued to 1000° C., whereupon 0.19 g. of water was injected into the outer silica jacket near the open end of the inner tube. Heating was continued for a period of about 90 hours at 1000° C. during which time fibrous crystals formed on the top edges of the boat containing the silica-aluminum-aluminum sulfide mixture near the end adjacent to the other boat.

At the conclusion of the heating period, the apparatus was cooled to room temperature and the boats removed. The boat containing the silica-aluminum-aluminum sulfide mixture had lost 0.27 g. and the other boat had gained 0.14 g. in weight. The fibrous crystals were removed and identified as mullite from their X-ray diffraction pattern. They were in the form of fine, curled ribbons less than 1 micron in cross-section and up to 8–10 mm. in length. These fibers are shown in FIGURE I (magnification 20×) from which the flexibility of the fibers is readily apparent. By touching a mass of the fibers with a needle, which was then withdrawn and rotated about its long axis, the entire mass could be spun into a thread in much the same manner as wool is spun.

EXAMPLE III

A milled mixture of silica, aluminum and aluminum sulfide in the proportions of 2:1:1 (by weight) contained in two alumina boats was heated in vacuum to a temperature of 920° C. as described in Example II. Argon was then admitted and heating was continued to a temperature of 1000° C. After 3 hours at 1000° C., during which time no fiber growth was observed, 10 cc. of hydrogen was injected into the tube and after an additional 2.25 hours of heating a further 10 cc. of hydrogen was injected. Sixteen hours later, fibrous crystals were observed to have formed between the top edge of the boats and the inner vitreous silica tube. Heating was continued for 72.5 hours additional, during which time further formation of fibrous crystals occurred. The fibrous product consisted of fine, spinnable, ribbon-like fibers up to 1.2 cm. in length, having the mullite crystal habit.

EXAMPLE IV

A mixture of silica, aluminum and aluminum sulfide containing SiO_2:Al:Al_2S_3 in the proportions 2:1:1 by weight was thoroughly mixed by grinding in a glass ball-mill for a period of 2 days. The fine powder so produced was placed in 2 alumina combustion boats which in turn were introduced into a silica reaction tube placed in an electric furnace. With continuous evacuation, the reaction tube was heated 16 hours at 800° C., following which the reactor was heated to 900° C. and argon was admitted to atmospheric pressure. The tube was heated to a temperature of 980° C., H_2 added to the argon to a concentration of 3% by volume and the heating continued for a period of 47 hours. Heating was then discontinued and the tube allowed to cool. The synthetic mullite fibers which adhered to the wall of the tube above the combustion boats containing the reactants were removed by picking with a wire probe. The majority of these fibers were about 1 micron in cross-sectional dimension and ranged in length up to 1–2 cm., i.e., the fibers ranged in axial ratio up to about 2000:1. Microscopic examination showed these fibers to be uniform and relatively free of dendrites, overgrowths and obvious

twinning. X-ray examination showed that the fibers were composed of aluminum silicate having the mullite structure as indicated by the data in Table I below. These fibers were carded, drafted and twisted to form a staple yarn as illustrated in FIGURE II (magnification 20×), which shows the zone in which fibers aligned more or less parallel by the carding and drafting operations are being twisted.

Table I

X-RAY PATTERN OF FIBROUS MULLITE [1]

Interplanar Spacing (A.)	Relative Intensity of Reflection [2]	Interplanar Spacing (A.)	Relative Intensity of Reflection
5.43	M	1.60	M
3.42	S	1.59	W
2.90	M	1.53	M
2.70	M	1.47	M
2.55	M	1.445	M
2.43	M	1.425	F
2.30	M	1.41	W
2.21	M	1.383	W
2.125	M	1.334	M
1.90	M	1.278	M
1.85	M	1.269	M
1.71	M	1.244	M

[1] In addition, the pattern contained four lines of moderate intensity attributable to silicon at 3.14, 1.92, 1.64 and 1.108 A. Eight weak lines were unassigned.

[2] The relative intensities are rated as follows: S=strong, M=moderate, W=week, F=faint.

The new spinnable mullite fibers of this invention are stable and refractory and reflect infrared radiation to a very high degree. These properties render the fibers, and threads, yarns and fabrics prepared therefrom, particularly useful in applications where a highly refractory, asbestos-type material is required, e.g., as thermal insulation, as a reinforcing component of ceramics, cermets and plastic films, as a component of paper and other fiber compositions, and as a filtering medium, particularly for high temperature applications.

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. As a new fibrous material, mullite having a fiber cross-sectional dimension of less than 5 microns, an axial ratio of at least 100:1, and sufficiently flexible to be spun.

2. As a new fibrous material, mullite having a fiber cross-sectional dimension of less than 5 microns, an axial ratio of at least 100:1, and in the form of spinnable flat ribbons.

3. As a new fibrous material, mullite having a fiber cross-sectional dimension of less than 5 microns, an axial ratio of at least 1000:1, and sufficiently flexible to be spun.

4. A method for preparing mullite in a form sufficiently flexible to be spun, which comprises heating a mixture containing sources of silicon, oxygen, aluminum, and sulfur in an atmosphere containing at least 1% hydrogen and at a temperature in the range of 800–1200° C., the relative proportions by weight of SiO_2:Al:Al_2S_3 derived from said sources varying from about 2:1:0.6 to 2:1:1, respectively, and crystallizing from the vapor phase derived by heating said mixture mullite fibers.

5. A method for preparing mullite in a form sufficiently flexible to be spun, which comprises contacting and reacting silicon dioxide, aluminum, and aluminum combined with a source of sulfur, in an atmosphere containing at least 1% hydrogen at a temperature in the range of 800–1200° C., said source of sulfur being a sulfur compound which on reaction with aluminum yields Al_2S_3, the relative proportions by weight of SiO_2:Al:Al_2S_3 ranging from approximately 2:1:0.6 to 2:1:1.

6. A method for preparing mullite in a form sufficiently flexible to be spun, which comprises contacting and reacting silicon dioxide, aluminum and aluminum sulfide in a ratio of 2:1:0.6–2:1:1, in an atmosphere containing at least 1% hydrogen and at a temperature in the range of 800–1200° C.

7. A method for preparing mullite in a form sufficiently flexible to be spun, as set forth in claim 6, wherein the relative proportions by weight of silicon dioxide, aluminum and aluminum sulfide are approximately 2:1:1 respectively.

8. A method for preparing mullite in a form sufficiently flexible to be spun, as set forth in claim 6, wherein the temperature is in the range of 900–1100° C.

9. As a thermal insulation, mullite having a fiber cross section of less than 5 microns, an axial ratio of at least 100:1, and sufficiently flexible to be spun.

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