

[54] **PRODUCT AND PROCESS**

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- [63] Continuation-in-part of Ser. No. 35,064, May 6, 1970, abandoned.
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[51] Int. Cl.: C23c 13/04
[58] Field of Search: 117/106 R, 106 A, 100 B, 117/121, 169 R, 169 A, 46 FA, 46 FC

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AD 438,145, "Silica Fiber Forming and Core-Sheath Composite Fiber Development," cover page, title page, ii, iii, 35,42,55-59.
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[57] **ABSTRACT**

High-strength fiber is prepared by coating a small grain, small diameter polycrystalline refractory oxide fiber with a specified amount of a glass-forming oxide or its precursor, and heating the coated fiber at a temperature sufficient to decompose the precursor to the oxide and/or to vitrify the oxide coating into an adherent, optically uniform, thin layer. The coating significantly increases the tensile strength of the fiber, while the fiber retains a substantial percentage of its original modulus. The fibers are especially suitable for reinforcement uses.

16 Claims, 2 Drawing Figures

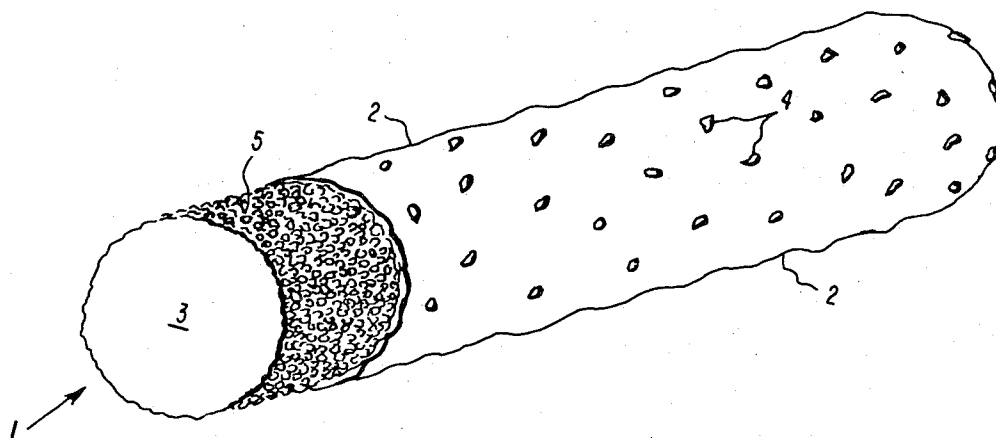


FIG. 1

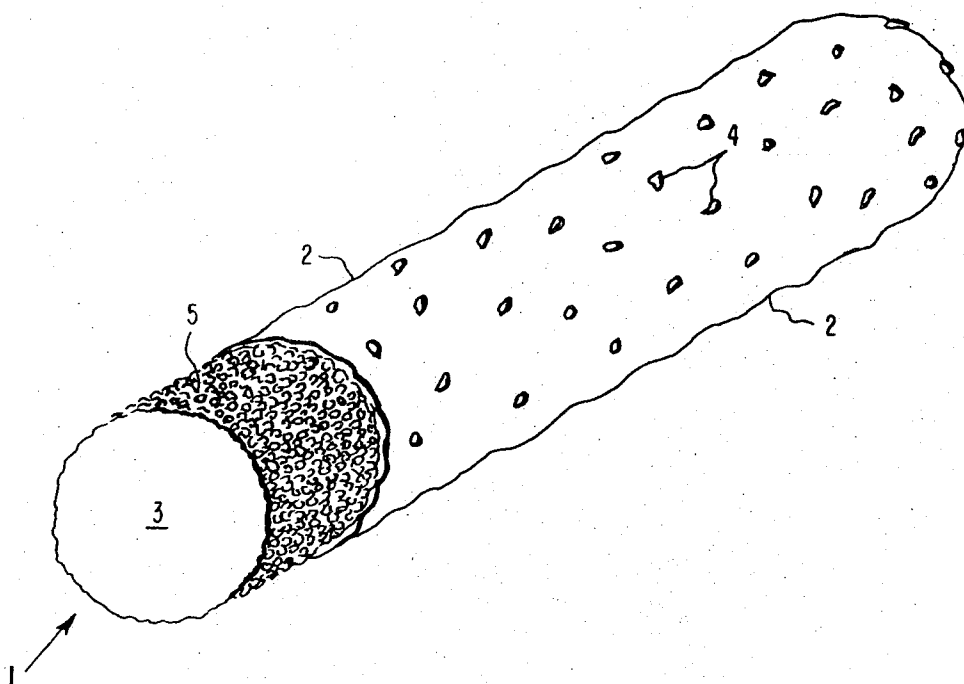
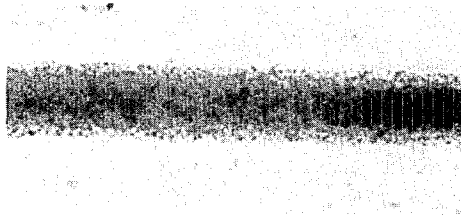
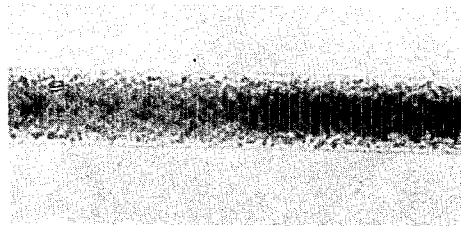


FIG. 2

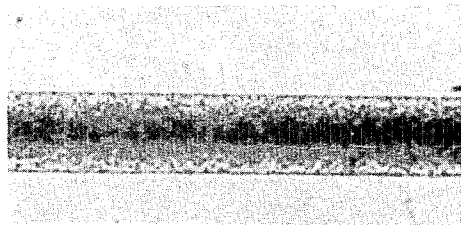
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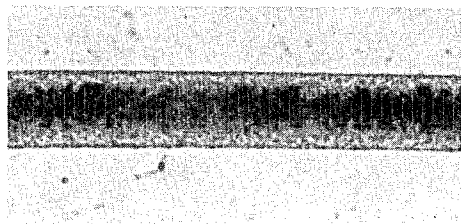
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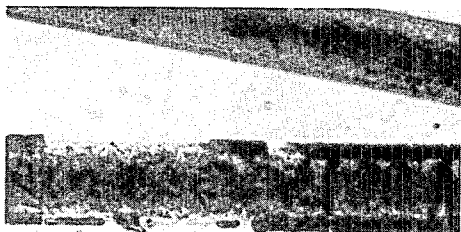
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PRODUCT AND PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 35,064, filed May 6, 1970 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to high-strength refractory fibers and to methods for preparing them.

2. Description of the Prior Art

Polycrystalline refractory oxide fibers, particularly alumina, of long lengths are very desirable due to the combination of high theoretical tensile strength and modulus with chemical inertness at ambient temperature and the retention of a substantial portion of these properties at temperatures above 1,000°C. Many efforts have been made to produce such fibers as shown for example in U.S. Pat. No. 3,311,689 to Kelsey and U.S. Pat. No. 3,327,865 to Blaze. However, previous fibers have only had a small fraction of the theoretical strength.

It has been proposed in publication AD 649,537 by the U.S. Department of Commerce to simultaneously extrude a polycrystalline oxide core and a glass sheath. This method has yielded small amounts of fibers with increased tensile strength but with low modulus.

SUMMARY OF THE INVENTION

The present invention provides high-strength fiber comprising a polycrystalline refractory oxide fiber having a fiber diameter between about 3 and 250 microns and comprised of grains having a median grain diameter of (1) less than about 3 microns and (2) less than about 10 percent of the diameter of the fiber, which has adhered to it a vitrified coating of a glass-forming composition comprising a glass-forming oxide, in the form of an optically uniform layer, the apparent thickness of the layer being (1) less than about 1 micron and (2) less than about 5 percent of the diameter of said fiber core.

The present invention also provides a process for preparing the high strength fiber described in the preceding paragraph which comprises applying a coating composition comprised of molecular to colloidal size particles of a glass-forming oxide or its precursor to the surface of a polycrystalline refractory oxide fiber also described in the preceding paragraph, said composition being applied in an amount sufficient to provide a vitrified layer (which results from the subsequent heating step) having an apparent thickness of less than about 1 micron and less than about 5 percent of the fiber diameter; followed by heating the coated fiber at a temperature and for a time sufficient to vitrify the coating into an adherent, optically uniform layer.

DESCRIPTION OF THE DRAWINGS

The invention may be better understood by reference to the accompanying drawings in which:

FIG. 1 illustrates a coated fiber of this invention; and

FIG. 2 is a series of photomicrographs illustrating polycrystalline refractory fibers before and after coating.

DESCRIPTION OF THE INVENTION

The Polycrystalline Refractory Oxide Fibers Used as the Substrate (or Core)

The term "fiber," used to denote the fibers of this invention as well as the fibers used as substrate, is used in the conventional sense, i.e., to mean a shaped article having a length greater than its diameter (e.g., a L/D ratio greater than 4/1, preferably greater than 10/1). This includes both continuous length structures (continuous filaments) and short lengths (staple fibers), preferably of substantially circular cross-section.

The term "polycrystalline" is used to mean that the fiber comprises numerous refractory oxide crystals rather than a single crystal. The term "refractory oxide" is used to mean an oxide that melts at least as high as 1,000°C. Such refractory oxides include Al_2O_3 , MgO , ThO_2 , ZrO_2 , Cr_2O_3 , Fe_2O_3 , NiO , CoO , Ce_2O_3 , UO_2 , BeO , HfO_2 , TiO_2 , La_2O_3 , and mixtures of oxides such as $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, $\text{Al}_2\text{O}_3 \cdot \text{AlPO}_4$, $\text{Al}_2\text{O}_3 \cdot \text{MgO}$, $\text{ZrO}_2 \cdot \text{SiO}_2$, $\text{ZrO}_2 \cdot \text{CaO}$, and $\text{ZrO}_2 \cdot \text{MgO}$.

A preferred fiber contains at least 60 percent by weight of a single simple refractory oxide, which is most preferably alumina. The remaining 0 to 40 percent comprises other refractory oxides which may be present as separate phases, as part of a compound or as a solid solution with another refractory oxide. Other oxides which are not considered refractory oxides, such as B_2O_3 , P_2O_5 , As_2O_3 , TeO_2 and SiO_2 may be present within the fiber in amounts that do not reduce the melting point of the final fiber below 1,000°C. Most preferably the preferred alumina fibers will contain only up to about 5 percent of one or more of the oxides of cobalt, magnesium, lanthanum, nickel, copper or cadmium.

The fibers are comprised of grains having a median grain diameter of less than about 3 microns and less than about 10 percent of the fiber diameter. Grains within this definition are believed to provide the fiber with a high degree of internal strength which is necessary to provide the maximum strength advantage of the fibers used in this invention.

Preferably, the porosity of the fibers is below 20 percent, most preferably below 10 percent. These low porosity fibers are preferred for use herein because they can be strengthened to a higher absolute level of strength when coated in accordance with this invention than fibers with a higher degree of porosity. Fibers which yield higher absolute strengths appear to have a relatively smaller number of internal flaws (pores and weak grain boundaries) as indicated by the amount of transgranular cleavage occurring upon fracturing. In contrast, fibers having lower strengths tend to cleave along grain boundaries when fractured (indicating more pores and more weak grain boundaries).

A generally preferred fiber for use in this invention has a porosity less than 10 percent, a crystallinity greater than 85 percent by weight and a grain size distribution wherein substantially none of the grains are larger than about 3 microns and at least 30 percent by weight are smaller than about 0.5 micron.

The fibers will have a diameter between about 3 and 250 microns, and preferably, because of ease of preparation, between about 5 and 125 microns. Most preferably the diameter will be between 6 and 50 microns.

The Vitrified Coating

The term "vitrified coating" as used herein means a coating that has been heated to melting or sintering and then cooled to form a glass-like coating.

The vitrified coating may be formed from a coating composition which contains an oxide, or a precursor of the oxide, as well as intermediates and modifiers and their precursors.

The term "glass-forming oxide" is used to mean any of the oxides, alone or in combination with other oxides, which can form a glass upon cooling from the liquid state. Suitable oxides include those which form glasses by themselves, i.e., "glass formers" (especially the oxides of silicon, boron, germanium and phosphorus), and combinations of one or more "glass formers" with one or more oxides known as "intermediates" and/or "modifiers" (see *Introduction to Ceramics* by W. R. Kingery, John Wiley and Sons, New York 1960, Chapter 5, and especially Table 5.1 listing "glass formers," "intermediates" and "modifiers"). Preferably the oxides should have a melting point above 800°C.

An "intermediate" is a compound which will not form a glass by itself, but is capable of being incorporated into the atomic networks that characterize polycrystalline glasses. A "modifier" is similar to an intermediate except that it does not form part of the network, but rather is believed to occupy interstices which occur in the atomic network. Suitable "intermediates" which can be used include: titanium dioxide, zinc oxide, lead oxide (PbO), and beryllium oxide. Suitable "modifiers" which can be used include: lithium oxide, magnesium oxide, calcium oxide, cadmium oxide, barium oxide, and strontium oxide.

The precursors of the oxides (i.e., materials which are converted to the oxides) include, for example, silicon tetrachloride (pure or partially hydrolyzed) or organosilicon compounds which are convertible to silica. Among the other suitable precursors may be named boron trichloride, boron tribromide, phosphorus trichloride, phosphorus oxychloride, germanium tetrachloride, and similar arsenic compounds. The particular precursor used should be selected in view of the ease of handling, the boiling point and the amount of the vitrified coating desired.

Coating compositions which contain at least about 50 percent precursors that will provide silica, are preferred, but even more preferred are those that will provide a vitrified coating that is substantially all silica.

Application of the Coating Composition to the Fiber

The coating composition may be in solid, liquid or vapor form when applied, and should be comprised of molecular to colloidal size particles. Since a majority of the suitable oxides, and any accompanying intermediates and modifiers that may be present are insoluble in water, they are readily applied as an aqueous dispersion of colloidal size particles of the oxide itself. For example, silicon dioxide, aluminum oxide, titanium dioxide, stannic oxide, germanium dioxide, zirconium dioxide, magnesium oxide and lead oxide (PbO) form relatively stable dispersions under suitable conditions (e.g., concentration, temperature and particle size).

Precursors of the oxides are generally more conveniently applied to the fiber as a liquid or vapor. This method of application is highly preferred in that bundles (e.g., closely aligned continuous filament tow) of uncoated fibers can be coated without the fibers sticking to one another (after coating or after firing). This lack of sticking is surprising since, generally, aqueous

colloidal dispersion coating techniques are only suitable for monofilaments (i.e., the fibers must be kept separated to prevent sticking). A useful method for coating fibers with a water-reactive precursor of silica such as silicon tetrachloride comprises exposing the fibers to an atmosphere, e.g., steam, wherein the relative humidity is greater than about 50 percent. The moist fibers are then passed through the liquid or vaporized silicon tetrachloride which reacts with water on the fiber surface to form a uniform layer of hydrated silica.

A preferred method for coating the fibers comprises passing the uncoated fiber, immediately after firing, into a bath that contains a solution or a dispersion of the precursor.

The coating composition may be applied to short (staple) fibers or to continuous lengths, individually or in groups (e.g., yarns or slivers) as described above.

A sufficient amount of the coating composition is applied to provide a vitrified layer having an apparent thickness of between about 0.01 micron and about 1 micron and less than about 5 percent of the uncoated fiber diameter. The actual amount of material applied depends on the form (vapor, liquid, solution, solid), concentration, and composition of the coating composition as well as the number of coating cycles.

It is preferred that relatively small amounts of the coating composition be applied to the fiber, i.e., just enough to provide a thin uniform coating.

Heating of the Coated Fiber

The oxides or precursors that have been applied using the methods set forth in the preceding section are vitrified by heating the fiber at a temperature above the melting or sintering temperature (e.g., greater than 1,100°C. for SiO₂), which is sufficient to vitrify the coating into an adherent, optically uniform layer. The term "vitrify" is used herein to mean that the heating conditions are sufficient to cause sintering or melting of the oxide. The particular temperature and time sufficient to vitrify a given coating composition may be selected from reasonably broad ranges with shorter times being satisfactory at higher temperatures. For example, amorphous silica may be vitrified when heated at a temperature of about 1,100°C. for many hours, when heated at a temperature of about 1,350°C. for about 30 seconds or when heated at a temperature of about 1,500°C. for about 5 seconds. Similar ranges exist for vitrifying the other oxides and are easily determinable. A preferred method for heating silica-coated fiber comprises passing the coated fiber through the flame of a propane-air torch (generally 1,500°C.-1,900°C., depending on the propane/air ratio) for a residence time in the flame of about 0.1 to 5.0 seconds.

During the heating process, in addition to vitrification of the coating material, precursors are converted to their respective oxides, and the water of hydration (of hydrated materials, if any) is driven off to form a substantially anhydrous coating. Additionally, any carrier liquid is volatilized and some volatile precursor may be vaporized.

It has been observed that if the heating step is omitted, the coating material is not vitrified as described above and the resultant fibers exhibit substantially no increase in tensile strength when compared with uncoated controls. Even if the coating material consisted of vitrified particles, vitrification in situ is still believed

to be necessary to provide the necessary adherence (discussed hereinafter) of the coating.

Although a variety of combinations of heating times and temperatures (as described above) may be used in the heating step, prolonged exposure or exposure at excessive temperatures has been observed to result in a loss of strength. This strength loss may be due to either a loss of the coating by volatilization or to diffusion of the coating into the fiber substrate.

The Coated Fiber Product of the Invention

The fiber coating is the vitrified oxide already discussed. A relatively thin layer of the coating (i.e., less than about 1 micron in apparent thickness, preferably less than about 0.1 micron), which is also less than about 5 percent of the fiber diameter, provides significant improvements in tensile properties. Because it is difficult to directly measure the thickness of these thin layers on the small diameter fiber substrates, the apparent thickness may be calculated from the amount of coating material on a large group of fibers and the density of the coating material as described later.

It has been observed in a series of coatings on the same fiber substrate that a significant increase in tensile strength in coated fibers over uncoated fiber substrates is obtained when the coating is at least about 0.01 micron thick and that the tensile strength increases as the coating thickness increases up to about 0.1 micron, after which the tensile strength decreases.

The preferred products of this invention will have a tensile strength of at least 100,000 pounds/square inch (psi) and more preferably at least 200,000 psi (i.e., 7,000 and 14,000 kilogram/cm² respectively). Preferred embodiments of this invention are also characterized by an elastic modulus (flexural) of at least 40,000,000 psi (2,800,000 kg/cm²).

Although the invention is not to be limited by the theoretical explanation thereof, it is believed that the coating "heals" small surface defects in the fiber surface and it is those portions of the fiber surface that must be coated. The required type of coating is assured by the thin optically uniform layer of material as described herein. It is further theorized that the surface defects result, at least in part, from the imperfect alignment of grains in the polycrystalline fiber at the fiber surface which creates asperities. It is therefore believed that to heal these defects, an apparent coating thickness of less than ½ the median grain diameter is desirable to fill or partially fill the asperities. When attempts are made to use larger amounts of coating, at least two problems arise. Firstly, spalling occurs, i.e., a degree or zone of coating thickness is reached whereupon the coating is no longer optically uniform due in part to its inability to withstand stresses (e.g., due to a differential thermal expansion) and the coating breaks away from the core. Secondly, if relatively thick coating (beyond the "zone of spalling") is applied there is a sacrifice in the desirably high modulus of the refractory oxide fiber substrate due to the lesser modulus of the coating (i.e., as the volume or thickness of the relatively low modulus coating increases, the modulus of the coated fiber decreases). It is therefore believed that both the "less than about 1 micron" and the "less than about 5 percent of the fiber diameter" characterizations of the apparent coating thickness are important herein; the former assures that the required coating uniformity to provide high tensile strength is obtained, while the latter restricts the volume of coating to approximately the

maximum required to completely fill asperities (since the median grain size is less than 10 percent of fiber diameter) and assures that the coated fiber retains the desired high modulus (the maximum volume of coating based on this restriction is 17.4percent).

The coating must adhere to the fiber substrate as described above, i.e., the coating must be optically uniform after being subjected to the cleaning procedures described hereinafter. The in situ vitrification (described hereinbefore) provides the desired adherence. It is believed that the coating layer is bonded to the fiber substrate through an interface (a product of a reaction between the coating and the fiber substrate). However, the interface is generally difficult to detect because it is so small.

FIG. 1 illustrates a coated fiber 1 of this invention. The coating 2 is in the form of an optically uniform layer of the required thickness adhered to the surface of the substrate 3. The coating 2 is not of constant thickness as illustrated (although it may be) and may or may not have small uncoated portions 4 which generally may appear at elevated points (generally protruding grains) on the fiber surface. The fiber segment which is uncoated illustrates the grains 5 of which the fiber is comprised.

Utility

The high strength (i.e., high tensile strength and high modulus) fibers of this invention are particularly useful as reinforcing agents for plastics, metals, ceramics and other materials. These fibers may be substituted for uncoated refractory fibers in various end-uses, especially where high tensile strength and high modulus are desired, e.g., filament-wound radomes and sonardomes, high temperature jet-engine vanes and support structures, and truss members in air frames.

A useful segment of a given fiber must be coated as described herein, i.e., the portion of the fiber that is stressed in use should be coated. If the particular end-use requires that the fiber be of uniform strength along its entire length, then the entire fiber surface should have the coating described above. On the other hand, if only segments of the fiber are subjected to stress in use, then only those portions need be coated.

For some applications such as filament-wound reinforced plastics and weaving, it may be advantageous to apply a sizing (e.g. starch) or a finish (e.g. a solution of gamma-amino propyl triethoxy silane) that will adhere to the filaments and be compatible with resins applied subsequently.

MEASUREMENT AND TESTING PROCEDURES

Presence and Uniformity of Coating

Method a

A substantially straight 2.5 cm.-long fiber sample is placed in a liquid exhibiting a refractive index which matches the refractive index of the substrate fiber (e.g., 1.760 for alpha alumina). The sample is examined using plane polarized white light, and a microscope with reasonably high numerical aperture optics (NA of about 0.85) and a magnification power of 600X. The fiber is positioned such that the longitudinal axis is substantially parallel with respect to the plane of polarized light. The image of the fiber-liquid interface is critically focused to obtain optimum resolution. The observation of a line that is substantially parallel with respect to the fiber axis and coextensive with the fiber-liquid interface indicates the presence of a coating on the fiber.

Observation of a substantially continuous line, indicates the coating is "optically uniform" to the degree that is considered necessary for the results of this invention, notwithstanding the fact that small portions of the fiber surface may be uncoated and/or that the coating may not be of constant thickness. If the sample does not show an optically uniform coating by this method it should be examined by method b.

Method b

A single fiber is mounted on a microscope slide and the fiber immersed in a liquid that matches the refractive index of the substrate fiber. The fiber and liquid are covered with a cover glass. The fiber is viewed at 1,000X (100X objective and 10X eyepiece) in oil immersion (cedar oil placed between the cover glass and objective to optimize resolution) on a Phase Contrast Microscope.

Briefly, a Phase Contrast Microscope converts optical path difference, which is the product of (thickness) and (index of refraction variation), into an intensity difference in black and white which is discernible by the eye as contrast in the image. Since the immersion medium matches the substrate fiber, contrast in the image is due to variations in the index of refraction of the areas exhibiting the contrast.

The fiber is scanned along its length in phase contrast and has an optically uniform coating if a random area exhibits continuous phase contrast along both edges in the entire field of view (approximately 0.1 mm at 1,000X). This method b is more sensitive and precise than method a and is preferably used.

Composition of the Vitrified Coating

The composition of the coating is determined by dissolving the coating material and analyzing the solution using conventional chemical analysis methods for the various elements.

Quantity of the Vitrified Coating

The amount of coating material present on the fiber substrate is determined by removal of the coating from a 0.5 to 1.0 gram fiber sample using a suitable etching agent that will dissolve the coating without substantially affecting the fiber substrate. For example, a 48 percent aqueous solution of hydrofluoric acid has been found satisfactory as an etching agent for silica coated alumina fibers. When etching is complete, any excess etching agent is removed by heating the sample to 900°C. This etching process is repeated until no weight difference is apparent following successive treatments. A weight correction equivalent is added to the observed weight loss to compensate for a weight change which has been observed when uncoated fibers are treated with the etching agent. For example, for the silica coated alumina fiber of Example 9, a correction of 0.03 percent is added to the observed weight loss.

As an example of another method, fibers of Examples 2, 3, 4 and 10 are fused with sodium carbonate; the melt dissolved in HCl and the solution diluted to a known volume. The concentration of silicon in the solution is obtained by using an Atomic Absorption Spectrophotometer (Model 303 by Perkin-Elmer Corp. of Norwalk, Conn.) and the weight of the coating calculated. See "Analytical Methods For Atomic Absorption Spectrophotometry" published by Perkin-Elmer, Norwalk, Conn., 1971.

Apparent Coating Thickness

The apparent coating thickness (μ , in microns) for a fiber of round cross section is calculated from the

amount of coating material per square meter of fiber substrate surface area and the density (d_c) in g/cc of the coating material using the following equation:

$$\mu = g/m^2 \times 1/d_c$$

- 5 The density (d_c) is determined by conventional means (a value of 2.19 g/cc is used for silica).

The quantity g/m^2 is calculated using the equation:
 $g/m^2 = DW/4V$

The fiber substrate diameter (D), expressed in meters, is measured using a microscope equipped with a filar micrometer eyepiece. V and W represent the volume (in cubic meters) and weight (in grams), respectively, of the fiber substrate sample.

The apparent coating thickness for nonround fibers can be calculated in an analogous manner using photomicrographs of the coated fiber or the substrate fiber to obtain the dimension of the substrate fiber.

Characteristics of the Coating

The vitrified nature of the coating is verified by testing the solubility of the coating in a liquid which is known to be a solvent for the coating in nonvitrified form. If the coating is vitrified, it will be substantially unaffected (as determined by the optical procedures previously described) under conditions which would dissolve the nonvitrified material. For example, if silica is the coating material, nonvitrified silica is removed during a two-hour immersion of the fiber in a 20 percent aqueous solution of sodium hydroxide at ambient temperature. Over the same period of time vitrified silica is substantially unaffected by this reagent.

The adherence of the coating to the substrate is verified by subjecting fiber having a substantially uniform coating (as verified by the optical procedures previously described) to a cleaning in a 0.1 percent aqueous conventional detergent (e.g., Tide) solution for 10 minutes at 50°C. with mild manual stirring. The fibers are rinsed and dried and then reexamined by the same optical procedures to determine whether the coating is still present.

Characteristics of the Fiber Substrate

Porosity of the fiber is calculated using the following equation:

$$\% \text{ Porosity} = (\text{Apparent Density} - \text{Bulk Density} / \text{Apparent Density}) \times 100.$$

The apparent density is obtained using an air pycnometer and a sample size of about 0.1 g. Prior to being evaluated the fiber is fired for 2 minutes at 1,500°C. The fiber is then pulverized using a mortar and pestle to produce lengths that are no more than five times the average fiber diameter thereby minimizing any closed void content in order to obtain an apparent density value which closely approximates or equals the true density of the sample.

The bulk density is the weight of fiber divided by the (area of cross-section $\times$ fiber length). Fibers are straightened in a propane-air flame for bulk density measurements in order that fiber length can easily be measured. Fiber lengths are measured using a microscope equipped with a micrometer and noting the displacement required to scan the entire length of the sample. The diameter of round fibers is measured with a precision of 2.5×10^{-4} mm. using a microscope fitted with a filar eyepiece. The area of noncircular cross-sections is measured using photographs of fiber ends. Fibers are weighed on a balance capable of weighing accurately to 1×10^{-7} gm. using a minimum sample of 1×10^{-5} gm.

The percent crystallinity of the fiber may be determined using the technique described by H. P. Klug and L. E. Alexander in "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," pp. 626-633, published by John Wiley & Sons, Inc., 1954. A suitable modification of this technique which is used to determine the amount of α -alumina present in preferred fibers of the invention is as follows (this procedure, with proper calibration, is applicable to all fibers of this invention):

A calibration curve for percent crystallinity versus X-ray intensity is obtained as described below.

Mixtures of α -alumina (100 percent crystalline) and glass (0 percent crystalline), both passing 325 mesh, are prepared containing 10 and 20 percent of the glass and homogenized using a mortar and pestle. The X-ray intensity for these mixtures and for 100 percent α -alumina is determined on an X-ray diffractometer equipped with a wide range goniometer, copper $K\alpha$ radiation, a nickel β filter, $\frac{1}{2}^\circ$ divergent and scatter slits, scintillation detector, and pulse height analyzer. The total amount (i.e., integrated) of diffracted intensity (I_A) from 12.00° to 45.33° (2θ) and the intensity (I_B) from 37.00° to 40.33° (2θ) is obtained using standard counting procedures as the sample is rotated at a rate of 2° (2θ) per minute, all analyses being carried out in duplicate. The intensity ratio $I_A:I_B$ is then calculated and plotted versus the percent crystalline material in the sample; the best straight line is drawn through the data points.

The same intensity ratio is measured for each of the fiber samples after they are ground to pass a 325 mesh screen and the percent crystallinity is then obtained from the previously determined calibration curve. The alumina fibers used as substrates in the examples have a percent crystallinity of 85 to 100 percent.

The grain size and size distribution on the longitudinal surface of the fibers is determined from an enlarged electron micrograph following an extension of the method of John E. Hilliard described in "Metal Progress," May 1964, pp. 99-102, and of R. L. Fullman, described in the "Journal of Metals," March 1953, p. 447 and ff.

An etch will be necessary to remove the coating and reveal the grains but should not substantially affect the grains themselves. As an example, alumina fibers coated with silica may be etched for 30 minutes in concentrated (48 percent) hydrofluoric acid at room temperature. Standard electron microscope procedure is used to obtain electron micrographs. Carbon is deposited directly on the platinum-shadowed etched (or unetched) fibers. The fibers are completely dissolved (hot phosphoric acid at about 350°C . being used for alumina fibers) from the carbon replica which is washed and examined on the electron microscope. A representative area is photographed at about 2,500 fold magnification. The negative is then enlarged to produce a photomicrograph that exhibits 20,000 fold magnification.

Three or four circles each having a radius of 6.4 centimeters, are drawn in different areas of the enlarged micrograph so that a total of at least 100 grains will be intersected by the circumferences of all the circles. The intersections of the circumference with each grain boundary intersecting the circumference are marked on all circles.

The length of the chord corresponding to the arc indicated on the circles for each of the grain intersections

is measured and the measured lengths are tabulated in the following fractions: 1-2 millimeters, 2-4 mm., 4-8 mm., 8-16 mm., 16-32 mm., and 32-64 mm.

The average chord length, $d_{(m)}$, for each of the size fractions can be calculated by dividing the sum of the chord lengths for the size fraction by the number of grains measured in the size fraction and converting to actual dimensions in the sample in angstroms. This is converted to average grain diameter, $d_{(a)}$ by the formula of Fullman:

$$d_{(a)} = \pi/2 d_{(m)}.$$

The average grain diameter and the percent of grains in each size fraction for a typical alumina fiber used in the examples follows: 0.16 μ (2%), 0.31 (11%), 0.47 (51%), 0.86 (34%), 1.57 (3%).

The size distribution data are plotted as cumulative percent vs. average grain diameter using log-normal probability paper (probability and logarithmic scales, the former based on the normal law of error). The best straight line is fitted to the data points between 10 and 98 percent. The average grain diameter corresponding to 50 cumulative percent on this line is the median grain diameter. A typical coated-alumina fiber of the examples has a median grain diameter of 0.43 (from above distribution).

Fiber Tensile Properties

Tensile strengths are measured at ambient room conditions using a method by R. D. Schile et al. in "Review of Scientific Instruments," 38 No. 8, August 1967, pp. 1103-4. The gauge length is 0.04 inch (0.1 cm.) and the crosshead speed is 1-4 mils/min.

Elastic moduli (flexural modulus) are measured by vibroscope techniques as described in J. Applied Physics, Vol. 26, No. 7, 786, 792, July, 1955.

Preparation of Refractory Oxide Fibers Used as Substrates

A preferred method as described in Offenlegungsschrift 1,913,663 of September, 1970, to Seufert, utilizes a two-phase spinning mix containing small particles of a refractory oxide such as alumina, zirconia etc. in an aqueous solution of a salt convertible to a refractory oxide upon heating (termed a "precursor of a refractory oxide"). Such spinning mixes may be concentrated and/or aged by heating (e.g., about 80°C .) to improve the ability of the spinning mix to be extruded and to aid in attenuating the extruded fiber. The spin mix is extruded through orifices and the extruded fiber attenuated to form as-spun fiber. The as-spun fiber is generally fired in two stages. The first or low temperature stage (e.g., heat slowly to 500° to 900°C .) removes the water and other volatile matter and may partially or completely decompose the precursor. The second or high temperature firing (e.g., $1,300^\circ$ to $1,500^\circ\text{C}$.) results in the formation of oxides, sintering of the oxide grains, and development of crystallinity. Optionally a final flame firing straightens the fibers and results in further grain growth and reduction of porosity. The fibers of Examples 1 to 9 are made by this technique.

U.S. Pat. No. 3,322,865 Blaze discloses the extrusion of viscous aqueous solutions of mixed metallic salts followed by firing to refractory oxide fibers. This general method is used for the starting fibers of Examples 10, 11 and 12.

Suitable fine particles of α -alumina (used in Examples 1-9) are made by classifying an aqueous dispersion (adjusted to a pH value of about 4.0 with hydrochloric acid) containing about 20 percent of finely divided alu-

minum oxide (XA-16, marketed by Aluminum Co. of America) by sedimentation to remove all particles larger than about 2 microns. The dispersion is concentrated to about 40 to 70 percent aluminum oxide. Using the procedure of G. A. Loomis (J. Amer. Ceramics Society 21 393, 1938) it is determined that about 100 percent of the particles in a typical classified product exhibit an equivalent spherical diameter less than 2 microns and about 89 percent exhibit a diameter less than 0.5 micron.

THE EXAMPLES

Parts and percentages in the following examples, as well as throughout this patent, are by weight unless otherwise stated.

The conditions used to make the starting fibers, i.e., the substrate fibers, for the examples are summarized in Table I. The ingredients of the spinning mix are mixed, well stirred, usually concentrated under vacuum, optionally aged at about 80°C. and extruded through spinnerets containing holes of about 0.05 mm. (Example 12), 0.1 mm. (all examples except 8 and 12) and 0.2 mm (Example 8) diameter.

In some cases (Examples 2, 6, 7 and 11) a finish of a 20/80 volume ratio of ethyl laurate in perchlorethylene is applied to the fibers before they are wound on a bobbin.

Table I gives the calculated composition of the spinning mix after concentration, the weight loss of the original mixture upon being concentrated and the firing conditions for the extruded fibers.

Oxide particle "A" is the classified alumina previously described. Oxide particle "B" are aluminum oxide-coated SiO₂ particles (Al₂O₃, 13.5%; SiO₂, 86.5%; Positive Sol 130M sold by the Du Pont Co. of Wilmington, Delaware).

Codes used for oxide precursors are as follow:

Al-1 aluminum chlorohydroxide dihydrate [Al₂(OH)₅Cl.2.2H₂O] from the solid compound

Al-2 Al₂(OH)₅Cl.2.2H₂O from a 50 percent aqueous solution of the aluminum chlorohydroxide complex

Al-3 basic aluminum acetate [Al(OH)₂(C₂H₃O₂)] from a 15.5 percent aqueous solution

Al-4 aluminum chloride from a 27.8 percent aqueous solution

Al-5 basic aluminum acetate [Al₂(OH)₅(C₂H₃O₂)] from solid hydrate containing 85 percent of this salt

Cr-1 hydrated chromium chlorohydroxide [Cr₅(OH)₆Cl₉.12H₂O] from the solid compound

Ca-1 calcium acetate monohydrate from the solid compound

Zr-1 zirconium acetate [H₂ZrO₂(C₂H₃O₂)₂] from a 44 percent aqueous solution

In addition, some examples contain parts of HCl (calculated as 100% HCl) as follows: 1 (0.38), 2 (0.32), 3a (0.13), 6 (0.4), 7 (0.38), 8 (0.43), and 9 (0.39). Example 11 also contains 0.25 part of acetic acid. Example 9 contains 0.1 part of a polyethylene oxide to increase the viscosity.

The fiber substrates used in Examples 3 b to f are made in a similar manner as 3a with the replacement of the cobalt salt as follows: b, NiCl₂.6H₂O (0.8 parts); c, MgCl₂.6H₂O (0.13 parts); d, CuCl₂.2H₂O (0.56 parts); e, La(NO₃)₃.bH₂O (1.4 parts); and f, CdCl₂.2.5H₂O (1.2 parts) and firing of 3c substrate

under conditions T1 and D2; all others fired under conditions T3, D2 and D3.

The concentrated spinning mixes of some examples contain small parts of MgCl₂.6H₂O as follows: 6 (0.54 parts); 7 (0.55), 8 (0.63), 9 (0.35) and 10 (1.6 parts).

Low temperature firing

Tunnel furnace

Fibers on a screen are carried on a belt through a tunnel furnace, 8 × 8 × 27-inch long interior (20 × 20 × 69 cm) at a constant speed such that the fibers are in the maximum temperature zone (6-inches long, 15 cm) for indicated time:

code	maximum temperature, °C.	time, minutes
T1	650	6
T2	650	1.25
T3	600	10.

Muffle furnace

Fibers in a platinum boat (M1 and M2) or on a refractory bobbin are heated in a muffle furnace as indicated

M1 slowly heated from room temperature to 550°C. where they are held for 45 minutes

M2 heated to 540°C. in one hour; then temperature raised at a rate of 280°C./hour to 820° to 870°C. where it is held for 5 to 10 minutes.

M3 heated to 550°C. and held for 45 minutes

M4 heated to 900°C. over a period of 4 hours

High temperature firing conditions

Tube furnace

Fibers in platinum boats are passed through a 36-inch (92 cm) long tube furnace at a constant rate such that they are exposed in the 6-inch (15 cm) long zone, midway of the open tube, of maximum temperature for the indicated time.

code	temperature of maximum temperature zone, °C.	time, minutes
D1	1500	1.0
D2	1500	2.0
D3	1500	10
D4	1400	0.5
D5	1350	1.0

Flame firing

Fibers are heated in a propane-air (propane-oxygen for F3) to the indicated temperature (by an optical pyrometer with no correction for Al₂O₃ emissivity) for the time given.

code	fiber temperature, °C.	time, seconds
F1	ca 1200-1400	1 to 2
F2	ca 1200-1400	3
F3	1450	about 1

Muffle furnace

M5 fibers on a refractory bobbin are placed in a cold muffle furnace and heated up to 1,300°C. over a period of 6 hours.

M6 fibers on a refractory bobbin are placed in a muffle furnace at 1,200°C., raised to 1,300°C. and held at that temperature for 90 minutes.

M7 fibers are heated in a muffle furnace at 1,300°C. for 2 hours.

Experience with many fibers indicates that the fired alumina fibers of the examples (all but Example 11) have median grain diameters of less than 3 microns and less than 10 percent of the fiber diameter and a crystallinity of at least 85 percent in view of the spinning compositions and the firing.

It is known (see U.S. Pat. No. 3,311,481) that fibers made as in Example 11 have very fine grain sizes that fulfill the requirements of this invention.

The fibers are heated by passing them at a rate of 0.4 ft./minute (0.12 meter/minute) through a 26 inch (66 cm.) long furnace wherein the thermal gradient is such that the temperature increases from ambient at each end to 650°C. midway through the furnace. The final stage of heating employs a 36-inch (92 cm.) long tube furnace wherein a 6-inch (15 cm.) long zone located midway along the length of the tube is heated to a temperature of 1,500°C., both ends of the tube being open

TABLE I

Example	Oxide Particles		Oxide Precursor		Weight Loss	Firing	
	Type	Parts	Type	Parts		Low Temperature	High Temperature
1	A	31.5	Al-1	44.0	1.5%	T2	D2
2	A	31.7	Al-2	43.6	34.8%	T3	D2
3	A	31.6	Al-2	43.7	32.4%	T1	D2,D3
4	A	11.7	CoCl ₂ ·6H ₂ O	0.80	32%	T2	D5
			Al-2	44.1			
			Cr-1	9.2			
			KCl	1.4			
5	(same as 2)						
6	A	31.3	Al-1	44.4	4.0%	M4	M5,F1
7	A	32.5	AlCl ₃ ·6H ₂ O	1.5	4.2%	M3	M6,F3
8	A	30.6	Al-1	46.2	1.9%	M1	M7,F2
			Al-1	43.4			
9	A	30.3	AlCl ₃ ·6H ₂ O	1.1			
10	none		Al-1	43.0	0%	T1	F1
			Al-5	47.6	32.4%	M2	D2, F1
			Al-4	8.8			
11	none		Zr-1	58.5	37.5%	T3	D1
12	none		Ca-1	5.0	25%	T3	F1
			Al-2	66.7			

EXAMPLE I

This example illustrates coated fibers of this invention and the effect of coating concentration.

A mixture comprising 1,193.8 g. of an aqueous aluminum oxide dispersion (73.5 weight percent solids), 23.6 cc. of concentrated aqueous hydrochloric acid and 384.4 grams of water is placed in a two liter capacity resin kettle equipped with a helical ribbon stirrer. The dispersion is simultaneously stirred and heated to 80°C., at which time 1,223.8 g. of solid aluminum chlorohydroxide, (atomic ratio of aluminum to chlorine = 2.01 to 1, equivalent aluminum oxide content = 42 percent by weight) are added. The resultant mixture is stirred and heated at 80°C. under atmospheric pressure for about 20 hours, during which time the salt dissolves. The dispersion is then allowed to cool to 26°C. with simultaneous deaeration under reduced pressure, which results in the loss of about 43 cc. of water. Continuous fibers are produced by extruding the deaerated mixture through thirty 0.004 inch (0.01 cm.) diameter by 0.05 inch (0.127 cm.) long spinneret holes using a pressure of 1,585-1815 p.s.i. ($1.1 \times 10^5 - 1.3 \times 10^5$ g./cm.²). The continuous fibers are collected using a bobbin that rotates at a peripheral speed of 365-450 ft. per minute (111-137 meters/minute).

Following completion of the extrusion, the fibers are cut on the bobbin by a blade moving in a direction parallel to the axis of the bobbin, and the fibers are collected as a multilayered, substantially unidirectional array.

to the environmental atmosphere. The fibers are moved through the furnace at a constant rate of speed such that their residence time in the 1,500°C. zone is two minutes. During this heating, any salts which are present are converted to their respective oxides and the oxide particles are sintered together to form a unitary polycrystalline refractory oxide fiber.

A representative sample of the fiber substrate (100 percent alumina) exhibits a tensile strength of 197,000 p.s.i. (1.38×10^7 g./cm.²), an elastic modulus of about 50×10^6 p.s.i. (3.5×10^9 g./cm.²), a porosity of less than about 5 percent, a crystallinity of greater than 85 percent, a median grain diameter of about 0.5 micron and a diameter of about 20 microns (0.8 mil.).

The fibers are heated to 1,500°C. for two minutes after which they are placed in a 2-inch (5 cm.) diameter glass tube and subjected to one or more cycles comprising (1) a five-minute exposure in a moist atmosphere produced by bubbling nitrogen at a rate of 6 cubic ft./hr. (0.168 meter³/hr.) through a water bath at a temperature of 50°C.; (2) a five-minute exposure in a silicon tetrachloride vapor atmosphere produced by bubbling nitrogen at a rate of 6 cubic ft./minute (0.168 meter³/hr.) across the surface of liquid silicon tetrachloride at ambient temperature. The liquid is stirred to increase the rate of evaporation. The coated fiber sample is washed in distilled water for 30 minutes, after which it is dried at 150°C.

The fiber is then heated at 1,500°C. for 12 seconds in a tube furnace to vitrify the coating. Analyses and the tensile strength of representative fiber samples are summarized in the following table.

No. of Cycles	Tensile Strength p.s.i. (g./cm. ²)	Elastic Modulus p.s.i. (g./cm. ²)	Quantity of SiO ₂ (g/m ²)	Apparent coating thickness (cal- culated) (Microns)	% of Fiber Diameter
0	197,000(1.38×10 ⁷)	50×10 ⁶ (3.5×10 ⁹)	0	0	0
1	262,000(1.84×10 ⁷)	50×10 ⁶ (3.5×10 ⁹)	0.05	0.025	0.1%
4	306,000(2.15×10 ⁷)	—	0.19	0.1	0.5%
7	309,000(2.17×10 ⁷)	—	0.20	0.1	0.5%
10	264,000(1.85×10 ⁷)	—	0.71	0.3	1.5%
13	209,000(1.47×10 ⁷)	—	0.80	0.4	2.0%

Each of the above coated fibers (except the fiber of the 13-cycle experiment) are characteristic of this invention; the coatings are vitrified, optically uniform layers of the required apparent thickness, adhered to the alumina fiber substrate. The above data show that the coating of this invention substantially improves the tensile strength of the uncoated fiber when even a very thin coating (0.025 micron) is present and that no further improvement results at thicknesses above about 0.1 micron. When the 0.3 micron thickness level is reached, it is noted that about 10 percent of the fibers do not have the coating uniformity required by this invention. However, the fibers that are properly coated, as required, do provide a substantial improvement as shown above. At this coating level, the apparent coating thickness of 0.3 micron is slightly less than the median grain diameter of fired coated fibers of this example. (A fiber of the 4-cycle experiment exhibits a median grain diameter of about 0.5 micron.) It is at approximately this degree of thickness that the zone of spalling is first reached as is evident from the nonuniformly coated 10 percent of the fibers. The fiber with a 0.4 micron thick coating illustrates a particular fiber from the batch which does not have the required coating uniformity of the products of this invention; the tensile strength of this fiber is considerably less than the other coated fibers reported.

This effect of the amount of coating on the uniformity of the coating is further illustrated for the above fibers by reference to FIG. 2. FIG. 2 is a series of photomicrographs obtained utilizing the method (a) for testing for presence and uniformity of coating. FIG. 2-A is a photomicrograph of an uncoated sample; this sample does not exhibit the lines, substantially parallel, with respect to the fiber-axis and coextensive with the fiber-oil interface, which would indicate the presence of a coating. Such lines are seen in FIGS. 2-B, 2-C and 2-D (which are photomicrographs of fiber samples of the above 1, 4, and 7 cycle runs); these lines are substantially continuous which indicates the required optical uniformity of the coating. FIG. 2-E is a photomicrograph of two different types of fiber samples of the same 10-cycle run as described above. The fiber in the upper portion of the figure is satisfactory and is quite similar to that of FIGS. 2-B, 2-C and 2-D, but the fiber in the lower portion is not satisfactory and is clearly distinct in that the observed line is discontinuous. These discontinuities are believed to represent the points of failure of the coating (e.g., where the coating has begun to spall off or fall away).

EXAMPLE 2

This example demonstrates additional types of silica precursors as coating materials.

307 g. of an aqueous dispersion containing 48.7 percent by weight of aluminum oxide particles is combined

with 415 g. of an aqueous solution of aluminum chlorohydroxide (Al/Cl = 1.84, equivalent to 23.6 percent by weight of aluminum oxide). The resulting mixture is homogenized using a domestic food blender, then heated for 20 minutes at 80°C., after which it is extruded to form continuous fibers at a rate of 450 ft./minute (138 meters/minute) using a spinneret with ten holes, 0.004 inch (0.01 cm.) in diameter and 0.050 inch (0.13 cm.) long. A finish comprising a 20/80 volume ratio mixture of ethyl laurate in perchloroethylene is applied to the filaments prior to their being collected on a bobbin. The fibers are removed from the bobbin as described in Example 1 and heated to 600°C. over 45 minutes after which they are allowed to cool to ambient temperature. The fibers are then fired for 2 minutes at 1,500°C. using the procedure set forth in Example 1.

A representative sample of the alumina fibers exhibits a tensile strength of 199,000 p.s.i. (1.40×10^7 g./cm.²), a modulus of about 50×10^6 p.s.i. (3.5×10^9 g./cm.²) a porosity of less than about 5 percent and a diameter of 19.5 microns.

Individual fibers are heated in a propane-air flame for between 2 and 4 seconds after which they are dipped into a 40° Baume aqueous solution of sodium silicate ($\text{Na}_2\text{O}/\text{SiO}_2 = 1/3.25$ which theoretically gives 76 percent by weight SiO₂ and 24 percent by weight Na₂O after firing) and then heated in a propane-air flame for about 1 second to vitrify the coating. The tensile strength of a representative coated fiber sample is 287,000 p.s.i. (2.02×10^7 g./cm.²) and the apparent thickness of the coating is 0.55 micron.

The coating procedure is repeated with the starting fiber using an aqueous solution of guanidinium silicate (prepared as disclosed in Example 1 of Yates, U.S. Pat. No. 3,475,375) and lithium chloride ($\text{Li}_2\text{O}/\text{SiO}_2 = 1/19$) which theoretically gives 95 percent by weight SiO₂ and 5 percent by weight Li₂O, after firing. After heating the coated fibers in a propane-air flame for one second to vitrify the coating, a representative sample exhibits a tensile strength of 305,000 p.s.i. (2.14×10^7 g./cm.²).

EXAMPLE 3

This example demonstrates fibers of this invention utilizing alumina fiber containing various modifiers.

415 g. of an aqueous solution of aluminum chlorohydroxide (equivalent to 23.6 percent by weight of aluminum oxide, and exhibiting a Al/Cl ratio of 1.86) is combined with 282 g. of an aqueous dispersion containing 53 percent by weight of alumina particles and 3.75 g. of solid cobaltous chloride hexahydrate. The mixture is homogenized using a domestic food blender, followed by concentration under reduced pressure to obtain a 32.4 percent weight loss. The concentrate is then heated for 20 minutes at 80°C. under atmospheric pressure. Fibers are obtained by extruding the resulting

mixture using a spinneret with nine holes, 0.004 inch (0.01 cm.) in diameter and 0.050 inch (0.13 cm.) in length. The fibers are fired as described in the following table.

The foregoing procedure is repeated, with the exception that other modifiers (nickel chloride, magnesium chloride, cupric chloride, lanthanum nitrate and cadmium chloride) listed in the following table are used in place of cobaltous chloride hexahydrate.

Individual fibers incorporating each of the modifiers are heated in a propane-air flame for between 2 and 4 seconds, then dipped once into an aqueous solution of guanidinium silicate, and heated for 1 second in a propane-air flame to vitrify the coating. Results are given in Table II.

The first coated fiber in Table II has a vitrified coating with an apparent thickness of 0.3 micron.

TABLE II

	% by Weight of Total Oxides Other than Alumina	TENSILE STRENGTH	
		Before Coating	After Coating
a	0.5 CoO	152,000 p.s.i. (1.07×10^7 g./cm ²)	344,000 p.s.i. (2.42×10^7 g./cm ²)
b	0.5 NiO	220,000 p.s.i. (1.55×10^7 g./cm ²)	382,000 p.s.i. (2.68×10^7 g./cm ²)
c	0.05 MgO	189,000 p.s.i. (1.33×10^7 g./cm ²)	353,000 p.s.i. (2.48×10^7 g./cm ²)
d	0.5 CuO	194,000 p.s.i. (1.36×10^7 g./cm ²)	372,000 p.s.i. (2.61×10^7 g./cm ²)
e	1.0 La ₂ O ₃	172,000 p.s.i. (1.21×10^7 g./cm ²)	344,000 p.s.i. (2.42×10^7 g./cm ²)
f	1.0 CdO	211,000 p.s.i. (1.48×10^7 g./cm ²)	393,000 p.s.i. (2.76×10^7 g./cm ²)

EXAMPLE 4

This example illustrates the use of alumina fibers which contain silica for the substrate in coated fibers of this invention.

The following materials were combined in a domestic food blender: 76 g. of a 45.4 percent by weight aqueous aluminum oxide dispersion, 66.3 g. of an aqueous dispersion comprising a 30 percent aluminum oxide-coated silicon dioxide particles [Positive Sol 130M; 87 wt. % SiO₂, 13 wt. % Al₂O₃, manufactured by Du Pont Company];

263 g. aluminum chlorohydroxide (Al/Cl atomic ratio = 1.86, equivalent to 23.6 wt. percent of aluminum oxide);

27.4 g. of solid chromium chlorohydroxide [Cr₅(OH)₆Cl₉·12H₂O]; and 4.2 g. potassium chloride. This mixture is stirred for 5 minutes, then concentrated by heating at 80°C. under a pressure of 95 mm. of mercury to obtain a weight loss of 32 percent.

A (Al₂O₃/SiO₂) fiber is extruded using a spinneret hole 0.004 inch (0.01 cm.) in diameter by 0.050 inch (0.13 cm.) long, and collected on a bobbin rotating with a peripheral speed of 700 ft./minute (210 meters/minute). The fibers are heated to 650°C. using the 650°C. furnace described in Example 1 and a fiber speed of 0.4 ft./minute (0.12 meter/minute), followed by a 1 minute exposure to a temperature of 1,350°C.

The fibers which contain 75.9% Al₂O₃, 13.2% SiO₂, 8.9% Cr₂O₃ and 2.0% K₂O with a diameter of about 17 microns, are heated for 2 minutes at a temperature of 1,350°C., after which they are allowed to remain for 2 hours in an atmosphere at 36°C. and a relative humidity of 95 percent. The fiber is then dipped momentarily into liquid silicon tetrachloride and the excess liquid

allowed to evaporate. Following a washing with distilled water and drying in air the coating is vitrified by exposing the fiber to a temperature of 1,500°C. for 5 seconds. The coating increases fiber tensile strength from 207,000 p.s.i. (1.5×10^7 g./cm²) to 259,000 p.s.i. (1.8×10^7 g./cm²).

EXAMPLE 5

This example illustrates the use of various types of vitrified coatings for fibers of this invention.

The fiber substrate is prepared using the procedure disclosed in Example 2. The fibers are heated in a propane-air flame for 2 to 4 seconds prior to being coated as described below.

Samples of these fibers are coated with the following coating compositions:

Fiber sample A is dipped once in a mixture of 9 g.

calcium chloride, 23 g. aqueous solution of aluminum chlorohydroxide (equivalent to 23.8 percent by weight Al₂O₃) and 15 g. distilled water.

Fiber sample B is dipped once in a solution comprising equal parts by weight of water and 85 weight percent phosphoric acid, and is then dipped once in a solution comprising equal parts by weight of calcium chloride and water.

Fiber sample C is dipped once in a mixture comprising 10 g. of an aqueous dispersion of colloidal particles of SiO₂ coated with aluminum oxide (Du Pont's Positive Sol 130M, containing 26 weight % SiO₂ and 4 weight % Al₂O₃) and 30.5 g. of an aqueous dispersion of colloidal aluminum oxide particles (Alon C) containing 24.2 percent by weight Al₂O₃.

The coated fiber samples are heated in a propane-air flame for about one second to vitrify the coating.

An uncoated fiber sample exhibits a tensile strength of 199,000 p.s.i. (1.4×10^7 g./cm²). The coated samples (A, B and C) exhibit tensile strengths of 269,000 p.s.i. (1.89×10^7 g./cm²), 259,000 p.s.i. (1.82×10^7 g./cm²) and 232,000 p.s.i. (1.63×10^7 g./cm²), respectively.

EXAMPLE 6

This example illustrates a continuous procedure for preparing the coated fibers of this invention.

Fiber Preparation

A spin mix is made by blending an aqueous slurry of Al₂O₃ particulate (60 percent solids) with solid "Chlorohydrol" Al₂(OH)₅Cl·2H₂O. The spin mix also contains a small amount of MgCl₂·6H₂O. The mix is transferred to a spinning cell and fibers are continuously spun. The fibers are drawn and a spin finish (20 percent ethyl laurate and 80 percent Perclene perchloroethylene) is ap-

plied thereto. The fibers are then wound up, under tension, on a refractory bobbin.

The fibers (on the refractory bobbin) are placed in a muffle furnace and heated to 900°C. over a period of 4 hours. The fibers are then placed in another muffle furnace and heated to 1,300°C. over a period of 6 hours. At this point the fibers have greater than about 100,000 p.s.i. tensile strength and can be easily handled without excessive filament breakage. The fibers are then removed from the bobbin and drawn at the rate of 10 ft./min. through a propane-air flame issuing from a 6-inch long ribbon burner. The apparent temperature, measured by an optical pyrometer (with no correction for Al_2O_3 emissivity at high temperature) is 1,300°C.

The resultant fibers (99.5% Al_2O_3 and less than 0.5% MgO) have an average tensile strength of 227,000 p.s.i. The median grain diameter is 0.47 micron.

Fiber Coating and Firing

The fibers (in continuous filamentary form) are continuously coated and fired by drawing them through the following zones at 15 ft. (4.55 m.) per minute: (1) Meker Burner (methane-air) flame zone approximately 1.5 inches (3.8 cm.) long; (2) Two inch (5 cm.) steam zone; (3) Three inch (7.6 cm.) long liquid silicon tetrachloride bath; and (4) A flame zone above a 1.5-inch (3.8 cm.) diameter surface burner supplied with a propane-air mixture through a 50-mesh per inch (per 2.54 cm.) stainless steel screen for a contact time of about 0.5 second apparent fiber temperature is approximately 1,060°C., measured with a Leeds and Northrup optical pyrometer, Model 8622C. However, no emissivity correction is applied so that the actual temperature is about 400° to 600°C. or more (depending upon the fiber and coating composition) greater than the indicated temperature.

The resulting fibers are silica coated according to this invention with an average tensile strength of about 264,000 p.s.i. (1.85×10^7 g./cm.²). The coating is

g./cm.²) and is in the form of a bobbin of yarn (735 denier) of 60 continuous filaments.

For coating, the bobbin of yarn is mounted horizontally on a spindle and the yarn drawn under a freely rotating pulley (polytetrafluoroethylene) submerged in the coating composition in an 8-inch (20 cm.) long bath and thence over 5 jets of nitrogen gas (adjusted to evaporate the bulk of any solvent diluent in the bath without breaking filaments in the yarn), thence about 0.25-inch (6.4 mm.) above a 1.5-inch (3.8 cm.) diameter surface burner supplied with a gas-air mixture through a 50-mesh per inch (per 2.54 cm.) stainless steel screen and wound on a bobbin at 15 feet (4.55 m.) per minute. In some cases the yarn is reheated at the same speed and omitting the bath which is indicated by multiple yarn temperature values in Table III.

Two poly(dimethyl siloxanes) in chloroform are used as the coating composition, A - (SF-99 by General Electric Co.) and B - (DC-200 by Dow Corning Corp.) having 10 and 100 centistokes viscosity at 25°C. respectively. Solutions in methyl chloroform are used.

Table III gives the bath composition (volume percent), the temperature to which the yarn is heated (by optical pyrometer using no emissivity correction), tensile strength of the final coated yarns after all indicated heat treatments and apparent coating thickness of the coated yarns.

All coated fibers in the Table except item g have an optically uniform coating by method b. Item g has a nonuniform coating apparently as a result of excessive coating.

A preferred process uses a bobbin of fiber as removed from the high temperature muffle furnace. The yarn is drawn vertically through an annular propane-oxygen burner and chimney over a finish roll where a 3 percent solution of silicone oil ("A" above) in trichlorethane is applied and then through a horizontal surface burner and wound up. Appropriate driving means, guides and tensioning devices are used.

TABLE III

Item	Bath Composition	Yarn Temp. °C.	Tensile psi $\times 10^{-4}$ psi (g/cm ² $\times 10^{-7}$)	Apparent Coating Thickness (μ)
a	0.25% A	1105°C.	24. (1.7)	0.01
b	0.25% B	1125	28. (2.0)	0.015
c	3% B	1110	29 (2.0)	0.035
d	10% B	1085, 1100	29 (2.0)	0.05
e	20% B	1105, 1110	30 (2.1)	.09
f	40% B	1165, 1140	30 (2.1)	0.2
g	100% B	1190, 1210, 1180	13 (0.9)	0.7

about 0.2 g./m.², which corresponds to an apparent coating thickness of about 0.1 micron.

EXAMPLE 7

This example illustrates a continuous process and the effect of coating thickness.

The alumina substrate fiber employed (containing about 0.2% MgO) has an average diameter of 22 microns and a tensile strength of 212,000 psi (1.49×10^7

EXAMPLE 8

Alumina fibers (containing about 0.24% MgO) with an average diameter of 48 microns are heated in a propane-air flame for about 3 seconds to sinter and straighten them.

The fibers are individually dipped in silicone oil (B of Example 7) and then held in the propane-air flame for about 1 second to obtain a coating of amorphous vitrified silica with an apparent coating thickness of 0.25

micron. The coated fibers have a tensile strength of 192,000 psi (1.35×10^7 g./cm.²) compared to the starting fibers of 121,000 psi (0.85×10^7 g./cm.²).

EXAMPLE 9

The starting alumina fibers (containing about 0.14% MgO) have a diameter of 8.7 microns and a tensile strength of 188,000 psi (1.33×10^7 g./cm.²).

The fibers are dipped once in guanidinium silicate solution of Example 2 and fired for about 1 second in a propane-air flame. The coated fibers have a tensile strength of 321,000 psi (2.26×10^7 g./cm.²).

EXAMPLE 10

The substrate alumina fibers (containing about 1.2% MgO) have a diameter of about 25 microns, a median grain diameter of 0.64 micron and a tensile strength of 140,000 psi (0.98×10^7 g./cm.²).

Individual fibers are dipped 3 times in a colloidal silica dispersion ("Ludox" HS-40) and then heated for about 2 seconds in the propane-air flame. The fibers with an apparent coating thickness of 0.06 micron have a tensile strength of 258,000 psi (1.82×10^7 g./cm.²).

EXAMPLE 11

This example illustrates the coating of a zirconia fiber.

424.7 g. of a 44% zirconium acetate ($\text{H}_2\text{ZrO}_2 \cdot (\text{OAc})_2$) solution in water, 15.8 g. of calcium acetate $\cdot \text{H}_2\text{O}$ and 0.8 g. of glacial acetic acid are mixed and placed in a round bottomed flask attached to a rotary evaporator. The flask is immersed in a 66°C. water bath and rotated slowly while a vacuum of 100–110 mm. Hg is applied. Evaporation is continued until 27.8 percent of the initial solution weight is removed (about 1 hr.). Foaming is excessive at this point so vacuum evaporation is stopped and evaporation is continued by passing a stream of dry nitrogen over the surface of the liquid in the rotating flask until a total of 37.5 percent of the initial solution weight is lost. The resulting viscous, bubble-filled solution is transferred to a centrifuge bottle and spun in a centrifuge until a clear solution is obtained. This solution has an equivalent oxide content of 35.7 percent. It is extruded through a 0.045 in. (0.11 cm.) long circular die orifice having a diameter of 0.004 in. (0.01 cm.). The fiber is allowed to drop through a column at ambient temperatures into an atmosphere of dry nitrogen and onto a bobbin which collects the fiber at a rate of 760 ft./min. (231 m./min.). Prior to the fiber being wound on the bobbin, it passes over a wick saturated with a spin finish comprising a solution of 20 percent by volume ethyl laurate in perchloroethylene. The fibers are removed from the bobbin by cutting across them parallel to the bobbin axis. The resulting sheet of fibers is placed in an oven at ambient temperature and raised to 600°C. in 45 min. The fibers are removed and heated for 1 minute at a temperature of 1,500°C. in a preheated tube furnace. The tensile strength of the fiber is 87,000 p.s.i.

The substrate fibers (95% ZrO_2) have a tensile strength of 87,000 psi (0.61×10^7 g./cm.²) and a diameter of 12 microns.

Individual fibers are coated by being dipped 5 times into an aqueous dispersion containing 30 percent by weight of colloidal silicon dioxide particles (Ludox colloidal silica AS). Following the completion of 5 dip-

pings, the fiber is heated in a propane-air flame for 2–5 seconds. The tensile strength is increased to 174,000 p.s.i. (1.22×10^7 g./cm.²).

EXAMPLE 12

This example demonstrates the use of fibers which have a porosity greater than 20 percent.

180 g. of an aqueous solution of aluminum chlorohydroxide (Al/Cl atomic ratio = 2; equivalent to 23.8 weight percent of aluminum oxide) is concentrated to obtain a weight loss of 25 percent. A fiber is extruded through a 0.002 inch (0.005 cm.) diameter spinneret hole. The end of the emerging fiber is secured to a spatula, which is moved away from the spinneret at a rate which yields a continuous fiber that is about 0.3 times the diameter of the spinneret hole.

Fibers are heated gradually to 600°C. over a 45 minute period, allowed to cool to ambient temperature, and then are placed in propane-air flame for 1–2 seconds. The fibers (about 100% Al_2O_3) have a porosity of about 30 percent.

After being reheated in a propane-air flame for between 2 and 4 seconds, short lengths of fiber are dipped 4 times in aqueous dispersion containing 30 percent by weight of colloidal silicon dioxide particles (Ludox AS). After completion of the dipping operation, the coating is vitrified by placing the fiber in a propane-air flame for about 1 second.

Coating improves the tensile strength of the fiber from an average value of 19,500 p.s.i. (0.14×10^7 g./cm.²) (average of 2 trials) to 63,000 p.s.i. (0.44×10^7 g./cm.²).

The preceding representative examples may be varied within the scope of the present total specification disclosure, as understood and practiced by one skilled in the art, to achieve essentially the same results.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

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

1. A high strength polycrystalline refractory oxide fiber having a diameter between about 3 and 250 microns and comprised of grains having a median grain diameter of

less than about 3 microns and

less than about 10 percent of said fiber diameter,

said fiber having adhered thereto a vitrified coating consisting essentially of a glass-forming oxide, in the form of an optically uniform layer, the apparent thickness of said coating being

less than about 1 micron,

less than about 5 percent of said fiber diameter and less than $\frac{1}{2}$ said median grain diameter.

2. The fiber of claim 1 wherein the refractory oxide fiber is at least 60 percent alumina by weight, based on the total weight of said fiber.

3. The fiber of claim 2 wherein the vitrified coating is at least 50% SiO_2 by weight, based on the total weight of said coating.

4. The fiber of claim 3 wherein the apparent thickness of said coating is between about 0.01 micron and about 0.1 micron.

5. The fiber of claim 4 wherein the porosity of the refractory oxide fiber is less than about 20 percent.

6. The fiber of claim 5 wherein the refractory oxide fiber has a porosity of less than 10 percent, a crystallinity of greater than 85 percent, and a grain size distribution wherein substantially none of the grains is larger than about 3 microns and at least 30 percent by weight are smaller than about 0.5 micron.

7. The fiber of claim 1 wherein said median grain diameter is about 0.5 micron.

8. The fiber of claim 1 wherein the vitrified coating is substantially 100% SiO₂.

9. The fiber of claim 8 wherein the apparent thickness of said coating is between about 0.01 micron and 1 micron.

10. The fiber of claim 9 wherein the refractory oxide fiber is substantially 100 percent alumina.

11. percent, plurality of the fibers of claim 10 in the form of a continuous yarn, each refractory oxide fiber having a porosity of less than 10 percent, a crystallinity of greater than 85 %, and a grain size distribution wherein substantially none of the grains is larger than about 3 microns and at least 30 percent by weight are smaller than about 0.5 micron.

12. Process for strengthening a yarn of polycrystalline refractory oxide fibers which comprises:

applying a coating to the surface of each fiber by advancing the yarn continuously through a fluid com-

position comprised of a precursor of a glass-forming oxide,

said fiber having a diameter between about 3 and 250 microns and comprised of grains having a median grain diameter of less than about 3 microns and less than about 10 percent of said diameter of said fiber, and

advancing the coated yarn to and through a heat zone, thereby heating each fiber to a temperature sufficient to convert said precursor to said oxide and to vitrify said coating,

the amount of precursor applied to the yarn being sufficient to provide said vitrified coating in an apparent thickness of less than about 1 micron and less than about 5 percent of said fiber diameter.

13. Process of claim 12 wherein said glass-forming oxide is silica, said precursor being applied in the liquid or vapor state.

14. Process of claim 13 wherein said precursor of silica is silicon tetrachloride.

15. Process of claim 14 wherein said heating is at a temperature of at least about 1,350°C. for less than about 30 seconds.

16. Process of claim 15 wherein said heating is at a temperature of between about 1,500° and 1,900°C. for about 0.1 to 5.0 seconds.

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