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[54] **CONTINUOUS FILAMENTS AND YARNS**

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[63] Continuation-in-part of Ser. No. 156,111, June 23, 1971, abandoned.

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[58] **Field of Search** ..... 161/172, 174, 178, 180; 106/65, 62, 73.4; 264/176 F, 210 F, 63; 57/140 R

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[57] **ABSTRACT**

Small diameter, but unusually strong polycrystalline alumina filaments are disclosed. They contain small randomly oriented grains, and contain a number of pores in which the volume of an average pore in the filaments is 600,000 cubic angstroms (A^3) or less, and at least 60% of the pores have a volume less than 500,000 A^3. The filaments have a diameter less than about 0.0008 inch. The filaments have a porosity of between 2 and 10% and are surprisingly strong, making them particularly adaptable for use as catalyst supports.

9 Claims, No Drawings

CONTINUOUS FILAMENTS AND YARNS

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my application Ser. No. 156,111, filed June 23, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to very fine, flexible continuous filaments and yarns and their preparation and more particularly alumina filaments and yarns.

2. Description of the Prior Art

Although alumina fibers have been prepared in the past, they have generally been either non-continuous, too large in diameter, too porous, too weak, or a combination of such. Thus, a need has existed for strong, continuous fine diameter alumina filaments to permit maximum utilization for reinforcement applications. Continuous filament yarns suitable for integrating with continuous processes for incorporating aligned reinforcing elements in plastics or metals have also been desired, and are provided by the fibers of this invention.

SUMMARY OF THE INVENTION

The present invention provides polycrystalline alumina filaments containing exceedingly small randomly oriented grains. The filaments have a diameter less than about 0.0008 inch, preferably about 0.0003 inch, and have a porosity of between about 2 and about 10%. A major proportion of the pores are exceedingly fine. More specifically, the volume of an average pore in the filaments is 600,000 cubic angstroms (A^3) or less, preferably less than 450,000 A^3; at least 60% and preferably at least 70% of the pores have a volume less than 500,000 A^3.

The chemical composition of the filaments is at least 80% by weight Al_2O_3 (preferably about 100%) with the predominant crystalline phase, i.e., 50% or more, as detected by X-ray diffraction, being alpha alumina. The remaining 20% or less consists essentially of one or more oxides of the type commonly associated with alumina.

Grain size of the fired filaments is exceedingly small, i.e., substantially all grains are less than 2 μ and preferably 90% or more of the grains are less than 0.5 μ.

"Continuous" is used herein in its normally accepted textile fibers definition of meaning a long filament of indefinite length.

The preferred filaments are selected from the following compositions: (1) substantially 100% Al_2O_3; (2) more than 99% Al_2O_3 and less than about 1% MgO; (3) about 84% Al_2O_3, about 15% SiO_2, about 1% Na_2O, about 0.25% MgO; and (4) about 94% Al_2O_3, about 5% SiO_2, about 1% alkali metal oxide, preferably Na_2O or K_2O, and about 0.25% MgO.

The most preferred product is a continuous filament yarn, preferably of at least 70 substantially straight, highly aligned α-alumina filaments, having the filament grains, diameter, pore size, and chemical composition limitations disclosed above.

DESCRIPTION OF THE INVENTION

The filaments of the present invention can be prepared by spinning a spinnable mix comprising:

1. substantially anhydrous alumina particles of generally spherical shape and exceedingly small size (i.e., colloidal) and comprising substantially 100% Al_2O_3; preferably gamma-alumina particles having a diameter ranging from about 0.005 μ to about 0.07 μ, the particles also preferably being selected in relationship to the desired diameter of the final filament such that the particles have a maximum diameter of not more than about 1% of the diameter of the final filament;

2. an aqueous phase having dissolved therein at least one precursor of alumina in the form of one or more basic aluminum salts, preferably aluminum chlorohydroxide having a basicity between 0.79 and 0.82; and

3. a high molecular weight water soluble polymer of ethylene oxide, preferably one having a viscosity above about 3,000 centipoises measured as a 5% aqueous solution at 25°C. (preferably 3,000 – 6,000 centipoises).

The alumina particles in the mix should provide 20 to 50%, preferably 35 to 45%, by weight of the total available oxides in the system; and the amount of alumina available from the alumina particles and precursor of alumina should be at least 80% of the total available oxide content of the system. The remaining 20% is preferably selected from other oxides as mentioned earlier. Preferably, the mix will contain from about 6 to 35% by weight of alumina particles.

Basicity of the salt may be calculated by dividing the number of hydroxyl anions by the total valence of aluminum cations in the empirical formula of the salt. Thus, aluminum chlorohydroxide has the approximate formula $Al_2(OH)_5Cl{\cdot}2H_2O$ for which basicity is five/six or 0.833. In the mix, this is adjusted to the desired value of 0.79 to 0.82 by addition, e.g., of HCl or $AlCl_3$.

The aqueous phase may optionally also contain precursors of other oxides or may contain other oxides as particles with the previously described particle size and percent limits. These oxides include SiO_2 and those of metals of Group IA, IB, IIA, IIIB, IVB, VB, VIB, VIIB or VIII of the Periodic Table or rare earths, e.g., oxides of La, Ti, V, Cr, Mn, Mo, Fe, Co, Ni, Mg, Pd, Pt, Cu, Ag, Ce, and also less than 3% by weight Li, Na, and/or K oxides.

One preferred particle is "Alon C" gamma-alumina manufactured by Cabot Corporation, having a particle size of 0.01 to 0.04 μ, as specified by the manufacturer. The particles are generally spherical in shape. The composititon of "Alon C" is about 100% Al_2O_3.

Another preferred particle is "Aluminum Oxide C" supplied by Degussa Inc. and having a particle size of 0.005 to 0.3 μ, as specified by the manufacturer. The particles are generally spherical in shape and their chemical composition is about 100% Al_2O_3. This is also gamma-alumina.

Aluminum chlorohydroxide is one of the most preferred precursors of alumina for use in this invention and has the approximate formula $Al_2(OH)_5Cl{\cdot}2H_2O$. Other basic aluminum salts which can be used as the precursor for alumina are basic aluminum nitrate and basic aluminum chloroacetate.

When up to 20% by weight of the total available oxides of the system are other than Al_2O_3, they may be introduced in the spin mix as solid particles within the

above defined size limits (e.g., colloidal silica) or may be added as precursors of the desired oxide, e.g., chromium chloride, nickel nitrate, iron chloride, cobalt chloride, or magnesium chloride.

It may be preferred to "age" some spin mixes to adjust viscosity. This is readily done by heating the mix under ambient pressure and at a temperature of about 80°C. The optimum aging time for a given mix appears to be a function of the initial solids concentration of the mix, and is in turn directly proportional to the length of time over which the aged system will remain extrudable at ambient temperature. If aging is continued until the mix becomes too viscous to extrude, more water may be added to adjust to the desired viscosity. The final viscosity of the spin mix is preferably about 100,000 to one million centipoises at 30°C. for good spinnability.

The polymer of ethylene oxide will be present in the spin mix in an amount of up to about 1% by weight of the total available oxides.

In a particularly preferred embodiment, for producing backwindable yarns of e.g., 75 or more continuous filaments each of about 0.003-inch diameter, one may use a spin mix of "Alon C" particles, aluminum chlorohydroxide, water, $MgCl_2 \cdot 6H_2O$, HCl and poly(ethylene oxide) [Polyox WSRN–3000; wherein 3000 refers to the viscosity in centipoises of the ethylene oxide polymer, measured as a 5% aqueous solution at 25°C.]. If desired, the mix may also contain colloidal silica (e.g., Positive Sol 130 M) in amounts to yield 4–15%, preferably about 10%, SiO_2 in the final filament, and alkali metal salts, preferably a potassium salt, in amounts to yield, e.g., 0.1–0.5% K_2O, Li_2O and/or Na_2O in the final fired filament.

The mix is preferably dry spun using orifices and throughput rates which minimize shear on the mix during extrusion through the spinneret. A preferred throughput rate for a spinneret having 0.006-inch diameter holes is 0.02 to 0.07 grams/minute/hole, i.e., 1.5 to 5 g/min. for a 75-hole spinneret. The spun filaments are attenuated, preferably at an attenuation ratio of 50–150 to 1 (volume ratio), e.g., by a pair of take-up rolls at the base of the spinning column (after application of a finish to the threadline, if desired); and wound up at the desired speed (e.g., 100–400 ft./min.) using a commercial windup machine (e.g., No. 959 Leesona Take-Up Machine).

A desirable commercial process involves taking up the spun yarn on a collapsible bobbin to form a shrinkable cake-like continuous filament package; firing the package at low temperature in a furnace, preferably by slowly raising the temperature from room temperature to about 550° –900°C., preferably 600°C., for a time sufficient to remove substantially all volatiles, with accompanying shrinkage of the package; subjecting the low-fired package to high temperature firing, between about 900° – 1,400°C., preferably to about 1,300°C. for about 2 hours; and preferably mounting the high-fired package on a freely rotating spindle, backwinding the multifilament strand therefrom, passing it through a heating zone preferably through a flame, e.g, from a propane/oxygen burner, at a filament temperature of 1,200°–1,400°C., for final sintering and filament straightening; and finally winding the flame-fired strand onto a final bobbin.

In forming the cake-like package, best results are obtained by using low winding tension [e.g., about 0.01 gpd] and the cakes are formed at a suitable wind angle (preferably about 13°) with a decreasing traverse stroke as the cake builds up so as to form a cake with edges that taper inward. A preferred cake has a 3½ inch inside diameter and 4 inch outside diameter, and any suitable width, e.g., about 6 inches.

The cake may be formed on a collapsible bobbin and removed therefrom during firing, but preferably, the cake is formed on a collapsible refractory bobbin on which the cake is kept during firing. A suitable collapsible refractory bobbin is made by rolling ¼-inch thick felt of refractory fibers (Fiberfrax Lo-Con-Felt) to form a cylinder, taping the cylinder with cellophane tape, and mounting it on a collapsible rolled cylinder, and then placing the whole assembly on the constant speed windup.

A spin finish such as one of 20% ethyl laurate and 80% Perclene perchloroethylene may be applied to the yarn between the attenuating rolls and the bottom of the spinning column, e.g., by drawing the yarn over a wick wet with the finish.

The cake-firing steps are preferably carried out by hanging the cake on a horizontal support (e.g., 1.8 inch O.D. alumina tubing) in the furnace and slowly raising the temperature of the furnace to the desired level. Low firing preferably involves raising the temperature from room temperature to about 550°–600°C. over a period of e.g., 1 to 2 hours and holding the cake at the final temperature for a time sufficient to remove all volatiles, e.g., 1 to 2 hours. Preferably a N_2 sweep is used around the cakes to facilitate removal of volatiles from the cake. High firing preferably involves placing the low fired cakes in a preheated furnace (e.g., at about 1,000°C.) and raising the furnace temperature to about 1,400°C., preferably 1,300°C. over a period of e.g., 1 to 2 hours and keeping the cake at the final temperature for a time (e.g., 1 to 2 hours) sufficient to strengthen the filaments to permit backwinding of the yarn from the cake.

In the flame-firing step, the furnace fired cake (optionally after cooling) is preferably mounted vertically on a freely rotating spindle and the yarn is backwound therefrom (e.g., at 20 fpm) so as to pass either horizontally or, vertically upward through a flame from a suitable source (e.g., propane-air; propane-oxygen; natural gas-air) to accomplish final sintering and straightening of the filaments.

CHARACTERIZATION TESTS

Tensile Strength

Filament tensile strengths are measured using a method 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 between 1 and 4 mils/minute.

Grain Size

The grain size and size distribution on the longitudinal surface of the fired shaped articles 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 R. L. Fullman, described in the "Journal of Metals," March 1953, p. 447 and ff.

A representative area photographed at about 2,500 fold magnification is enlarged about 10,000 fold.

Three or four circles each having a radius of 6.4 centimeters, are drawn in different areas of the enlarged

micrograph. The exact number of circles is chosen so that at least 100 total grains will be measured. The scale conversion factor is 1 millimeter representing 0.05 micron. The intersections between grain boundary and circle are indicated at all points around the circumference of the circles. The intersections of the circumference with grain boundaries are marked on all circles in the above manner.

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 distribution of grain sizes can be calculated from the number of chord lengths below a series of specified sizes.

The total length of chords is obtained by adding together all the chords measured for a given group, and when divided by the total number of grains yields an average chord length as measured for a grain on the fiber surface. The average chord length for each of the size fractions can be calculated by dividing the total chord length for the size fraction by the number of grains measured in the size fraction. Multiplying these average lengths $d_{(m)}$ by the scale conversion factor of 0.050 micron per millimeter converts the average chord lengths to microns. This is converted to average grain diameter, $d_{(a)}$ by the formula of Fullman:

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

Porosity

Porosity is estimated from the apparent fiber density determined as described below and the known density of α-alumina, 3.98 g./cc.

$$\% \text{ porosity} = (3.98 - \text{apparent density})/(3.98) \times 100$$

To determine apparent density, a fiber sample is placed in a holder suspended from the arm of a balance. Four weighings (described below) are made and these together with the density (E) of perchlorethylene at the temperature during the determination are used to calculate the apparent density.

$$\text{Apparent density} = [(A-C)E]/[A-C+D-B]$$

A — weight of holder + sample in air

B — weight of holder + sample immersed in perchlorethylene

C — weight of holder in air

D — weight of holder immersed in perchlorethylene

Diameter

Filament diameter is measured with the aid of a microscope equipped with a filar micrometer eyepiece.

Microporosity Measurements

Volume of the average pore and % pores less than 500,000 A^3 are determined as follows.

Parallel fibers are embedded in epoxy resin in standard mounting molds to obtain a hard mount, e.g., Ciba Epoxy 910. The mounted fibers are pretrimmed to specimen widths that contain 1–12 fibers for cross section ultramicrotomy. The trimmed specimen is mounted in an ultramicrotome (e.g., Porter-Blum MT-2, LKB Ultratome) and sectioned with a diamond knife. An instrument thickness setting of 400 to 800 A is used and the knife is operated at a slow speed of 0.5 mm./sec. The sections are caught on the surface of a 10 vol. % solution of acetone in triple distilled water and supported for examination on 100 mesh carbon-coated copper grids.

If the sections are thin enough (about 1000 A) they are observed by transmission electron microscopy at 100 KV. (Thicker sections up to 10,000 A may be observed in higher KV capability electron microscopes). Representative areas are micrographed of magnifications at 15,000 – 50,000×. The electron micrographs are enlarged and printed to give prints of representative areas (minimum of six) at final magnification of 100,000×.

Representative 100,000× prints of each sample are examined. The diameters of pores are measured, using a measuring magnifier with a scale marked in 0.1 mm. increments. Individual pore diameter measurements are made to the nearest 0.1 mm. and recorded. A minimum of 250 pores per sample are measured from at least six different areas per sample and from at least four different fragments of filament cross section per area. The pore volume, assuming spherically shaped pores, is calculated from the diameter measurements from $V = 1/6\ \pi d^3$ where d is the pore diameter in angstroms; the distribution is plotted (as "% finer than" vs. "pore volume") and the % of pores smaller than 500,000 A^3 is recorded; and the average (arithmetic average) pore volume is determined and recorded in cubic angstroms.

Critical Dimension of X-ray Scattering Sites

The preferred fibers of this invention exhibit X-ray scattering sites having a critical dimension of 75A. or less. The critical dimension of the X-ray scattering sites in the filaments is determined by low angle X-ray scattering techniques. This method measures pore size and/or microstructural defects (when present) for the fibers of this invention in the absence of other centers of large electron density gradients such as discrete phases of heavy metals or their oxides. The procedure used involves obtaining a low angle diffraction pattern as follows:

Prepare a 10 mil thick sample of fibers and mount on a 15 mil diameter pinhole mount. Place sample holder in the end of the collimator inside the vacuum flat-plate camera. The filaments are placed at an angle of 45° to the horizon.

A standard film cassette is loaded with two sheets of film and placed in the 32 cm. slot (sample to film distance) and the camera is evacuated. The shutter is opened and the exposure is made for 24 hours.

The cassette is removed from the camera after exposure and the film removed and processed by standard procedures.

Densitometer traces of the diffuse scattering patterns on the film closer to the sample are obtained as follows:

Inspect the diffuse scatter pattern to ascertain its symmetry. For products of this invention, the pattern will be circular. The X-ray film is placed on the densitometer stage such that the traverse is at about 45° to an edge of the film and passes through the center of the hole in the film. A densitometer trace (using e.g., a Joyce Loebl Double Beam Recording Microdensitometer MK III C) is obtained from the film using a suitable density wedge (use the same wedge for all films scanned to insure equidensity traces). A magnification and lever ratio are chosen (e.g., 5×, 10:1) to insure obtaining a full trace with sufficient baseline for subsequent measurements. More than one lever ratio may be used as a check on baseline estimation. The film is then rotated 90° and a second trace is obtained. The proce-

dure is repeated once more at the two different traverse-film edge orientations to result in a minimum of 4 densitometer traces per film.

A baseline is drawn for each trace. Tangents to the trace at full scale are drawn to intercept the baseline and the distance between these two intercepts is measured in mm (corrected for magnification). The four distances per sample are tabulated and the average of the four is determined. Using suitable standard conversion tables for 32 cm. sample to film distance, the average measurement is tabulated in Angstrom units; this is recorded as the critical dimension of the X-ray scattering sites.

The distance between the intercepts at the baseline represents the critical dimension of the scattering sites that make a significant contribution to the diffuse low angle X-ray scattering pattern.

Optical Orientation Test

Sample fibers are immersed in a 1.76 refractive index immersion oil and observed under crossed polars in a polarizing microscope with the Gypsum ("Red One") plate inserted. The specimen is rotated from the +45° to the −45° position and observation of the colors and their changes upon rotation are recorded. For a fiber to exhibit random optical orientation of the grains, the filament must not show any uniform change from yellow to blue or blue to yellow along its length upon rotation of the specimen. For samples with poor transmission properties, the criteria are still met if the filament edges (where good transmission occurs) clearly exhibit the lack of uniform color changes. The fibers of Example 1 were examined in this way and do not show uniform change in color, i.e., they contain nonuniform (randomly) oriented grains.

Crystalline Orientation: X-ray Determination

Two different sample mountings are required to determine if there is crystal orientation in the fiber. The mounting procedures are:

1. Flat mounting: Fibers are placed in a holder so that the fiber axes are parallel to the X-ray beam when the diffractometer is at 0° 2θ with fiber ends pointing toward the tube and detector.

2. End mounting: A thick parallel bundle of fibers is embedded in epoxy; 3 mm. sheets are cut therefrom perpendicular to fiber axis and placed in a holder or a bundle of aligned fibers is placed directly in a tubular holder so that the fiber axes are perpendicular to the X-ray beam when the diffractometer is at 0° 2θ.

Each sample holder is placed on an X-ray diffractometer equipped with a wide range goniometer, copper Kα radiation, a nickel filter, ½° divergent and scatter slits, scintillation detector, and pulse height analyzer.

Diffractometer scans are made for each sample preparation from 66° to 70° and 75° to 79° 2θ using the X-ray equipment described previously and operating at a scanning speed 1° 2θ/minute, chart speed 1 inch/minute, time constant 2 and recorded range set at one value so that both peaks [(030) and (1.0.10) respectively] will be on scale. A baseline is drawn below each peak and the height of the peak above background is determined. A ratio of the peak intensities [(030)/(1.0.10)] is calculated for the two scans.

Crystalline orientation as used herein is present in the fiber if the intensity ratio [(030)/(1.0.10)] of the flat mounting differs from the intensity ratio [(030)/(1.0.10)] of the end mounting by at least 1.0 unit.

Results for Example 1 are given below:

Mounting	Intensity Ratio [(030)/(1.0.10)]
Flat	3.1
End	2.7

The results for Example 1, wherein the difference is 0.4 indicate that crystal orientation is not present.

EXAMPLE 1

This example illustrates preparation of yarn from "Alon C" particles.

A spin mix is made by blending 770 gms. of water, 10 gms. of $MgCl_2 \cdot 6H_2O$, 150 gms. of $AlCl_3 \cdot 6H_2O$ and 15 gms. of concentrated HCl (12 N) in a 2-liter mixing vessel ("Hastelloy B;" height to depth ratio = 1). The vessel is sealed, placed in an 80°C. bath and stirred for 30 minutes. To this 500 gms. of "Alon C" alumina particulate, having a diameter of about 0.03 microns, is added and the mixing speed is increased from 200 rpm to 300 rpm. Mixing at this speed is continued for 45 minutes. As 1,200 gms. of alumina precursor, solid "Chlorhydrol" $Al_2(OH)_5Cl \cdot 2.2H_2O$ are slowly added (viscosity increases), the mixing speed is slowly increased to 400 rpm. After 1 hour, mixing speed is reduced to 300 rpm. and mixing is continued overnight. The stirrer is then stopped and 130 gms. of a 10% solution of WSRN–3000 "Polyox" (sold by Union Carbide) is added to the spin mix. Mixing is continued for 30 minutes. The vessel is then placed in a 20°–30°C. bath and the mixing speed is reduced to 100 rpm. and vacuum is applied to the vessel for simultaneous deaeration and cooling. During this step, water is removed and the viscosity of the spin mix increases. A small change in the water content (about 0.5 weight %) changes the viscosity of the mix about 2,000 poises. Viscosity is monitored by measuring the power output of the stirrer motor; as the spin mix viscosity increases during cooling and deaeration, power is increased to maintain constant stirrer speed. Spin mix viscosity is controlled to ±500 poises. In this example, a spin mix viscosity of 4,000 poises at 26°C. is obtained by releasing the vacuum after a power reading of 88 is obtained for a full 100 full scale deflection on the Esterline-Angus Model A601C meter. At this point, the spin mix is transferred to a spinning cell (2.66 inch inside diameter and 17 ¼ inch long) by connecting the mixing vessel to the cell and drawing the mix into the cell by vacuum. After charging the cell, a nylon plug having an air purge valve, is placed in one end of the cell and a spinneret, cap and filter assembly fixed to the other end.

The filter assembly consists of the following (in order of flow through the filter):

a. 6 oz/yd^2 continuous filament polyester bonded nonwoven fabric filter prepared in accordance with the general teachings of U.S. Pat. No. 3,341,394
b. needle-punched polypropylene felt filter (0.15 inch thick; 20 micron)
c. two additional filters as described in (a) above
d. 50-mesh stainless steel screen
e. titanium distribution plate serving to distribute the spin mix uniformly to the spinneret.

The spinneret has 75 holes (each 0.006 inch in diameter and 0.050 inch long) arranged in concentric circles, there being 30 holes equally spaced on a 2½ inch diameter circle, 20 holes equally spaced on a 2 inch di-

ameter circle, 15 holes equally spaced on a 1½ inch diameter circle and 10 holes equally spaced on a 1 inch diameter circle.

The cell, fitted with the spinneret and nylon plug, is mounted at the top of a 9-ft. long spinning column and pressure is applied to the nylon plug by a hydraulic ram. At a ram pressure of 80–90 psi (300 psi cell pressure) filaments are extruded through the spinneret with a total mix flow rate of 1.5 gms/min. An air sweep of 10 scfm at 125°C. is introduced at the top of the spinning column and the column air temperature is maintained at 58°C. with a spinning cell temperature of 32°C. A relatively humidity gradient is maintained (1.5% at the top to 12% at the bottom of the column). The filaments are drawn at the bottom of the column by two attenuating rolls mounted one above the other — both rotating at a surface speed of 100 fpm. The 75 filament yarn is drawn around the outside of the two 6 inch diameter rolls for 4 wraps and then wound up under a tension of about 2–5 grams on a collapsible refractory "Fiberfrax" bobbin of the type described hereinbefore mounted on a constant speed windup. A spin finish is applied as described hereinbefore. A cake package is collected in a 20-min. period. The cake package, on its refractory bobbin, is placed in a muffle furnace and heated from room temperature to 550°C.; it is kept at 550°C. for 60 minutes; total time in the furnace is about 130 minutes. It is then placed in a second muffle furnace which is at 1,040°C. and the temperature is raised to 1,300°C. The package is kept at 1,300°C. for 60 minutes. Total time in the furnace is about 130 minutes.

At this point, the yarn can be handled without excessive filament breakage. The bobbin of yarn is mounted vertically on a freely rotating spindle and drawn horizontally through a natural gas-air flame (about 1 inch wide) issuing from a modified Fisher burner. The resultant filaments have an average tensile strength of 225,000 psi measured at 1/25 inch gage length on individual filaments. Single filament diameter is 0.0003 inch. The filaments have grains, 90% of which are finer than ½ micron in size, and an average pore volume of 438,000 A^3. From 70 to 75% of the pores are less than 500,000 A^3 in size. The critical dimension of the scattering sites is 75 A. The alumina in the final filaments is α-alumina. The fibers have a porosity of 7.5%.

Another suitable spin mix can be made as follows: Ten grams of $MgCl_2 \cdot 6H_2O$, 100 gms. of $AlCl_3 \cdot 6H_2O$, and 10 gms. of NaCl are placed in a 2-liter mixing vessel ("Hastelloy B;" height to depth ratio = 1). To this, 300 gms. of water and then 800 gms. of Positive Sol [which is a 30% solids (26% SiO_2, 4% Al_2O_3) aqueous dispersion of alumina coated SiO_2 particles (diameter about 16 Mu) sold by E. I. du Pont de Nemours and Company, Inc.] are added and the vessel is sealed, placed in an 80°C. bath and stirred for 30 minutes. to this, 450 gms. of "Aluminum Oxide C," gamma-alumina, from Degussa Inc., having a particle size range of 0.005 to 0.03 μ are added and the mixing speed is increased from 200 rpm. to 300 rpm. Mixing at this speed is continued for 45 minutes. As 1,200 gms. of alumina precursor, solid "Chlorhydrol" $Al_2(OH)_5Cl \cdot 2.2H_2O$, are slowly added (viscosity increases), the mixing speed is slowly increased to 400 rpm. After one hour, mixing speed is reduced to 300 rpm. and mixing is continued for 67 hours at 80°C. The stirrer is then stopped and 150 gms. of a 10% solution of WSRN–3000 "Polyox" sold by Union Carbide (a high molecular weight polymer of ethylene oxide, having a viscosity of 3,000 centipoises measured as a 5% aqueous solution at 25°C.) is added to the spin mix. Mixing is continued for 30 minutes. The vessel is then placed in a 20°–30°C. bath and the mixing speed is reduced to 100 rpm. and vacuum is applied to the vessel for simultaneous deaeration and cooling. During this step, water is removed and viscosity of the mix increases. A small change in the water content (about 0.5 weight %) changes the viscosity of the mix about 2000 poises. Viscosity is monitored and controlled as in Example 1. When the spin mix has a viscosity of 300,000 centipoises at 26°C. it is transferred to a spinning cell (2.66 inch inside diameter and 17.25 inch long) by connecting the mixing vessel to the cell and drawing the mix into the cell by vacuum. After charging the cell, a nylon plug, having an air purge valve, is placed in one end of the cell and a spinneret, cap and filter assembly fixed to the other end. The mix can then be spun as described hereinabove in this example, and fired until α-alumina filaments are obtained.

The fibers of this invention are useful as reinforcing fibers for metal, thermoset resins, and plastic composites for structural applications such as turbine blades, helicopter rotors and printed circuit boards. Their thermostability also makes them useful as catalyst supports and high temperature insulation. Their porosity is in general very low. In general, the lower the porosity, the stronger the fiber. In addition, however, it is unusual that fibers of the strength of those described herein may have a porosity of7.5 or 10%. Thus, the fibers are particulary useful as ceramic catalyst supports in applications where they are especially subject to stress.

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

1. A continuous polycrystalline alumina filament having a diameter less than about 0.0008 inch which contains randomly oriented grains having a size less than 2 microns, at least about 90% of said grains having a size less than 0.5 micron; said filament having a porosity of between about 2 and about 10% and containing pores having an average volume each of less than 600,000 cubic angstroms, with at least 60% of the pores each having a volume of less than 500,000 cubic angstroms; said filament being at least 80% by weight Al_2O_3 with the predominant crystalline phase, as detected by X-ray diffraction, being alpha alumina.

2. The filament of claim **1** wherein the average volume of each pore is less than 450,000 cubic angstroms, and at least 70% of the pores have a volume of less than 500,000 cubic angstroms each.

3. The filament of claim **2** wherein the filament diameter is about 0.0003 inch.

4. The filament of claim **1** wherein the filament is substantially 100% α-alumina.

5. The filament of claim **4** which contains up to about 1% by weight magnesium oxide.

6. The filament of claim **1** which contains between about 1–20% by weight silica, in addition to the alu-

mina, up to 3% of an alkali metal oxide, and up to 1% of an alkalineearth metal oxide.

7. A yarn comprising at least 70 filaments defined as in claim **1.**

8. A yarn comprising at least 70 filaments defined as in claim **4.**

9. A yarn comprising at least 70 filaments defined as in claim **6.**

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