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(54) **CERAMIC OXIDE FIBERS**

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(57) **ABSTRACT**
Tow of substantially continuous ceramic oxide fibers having
a sizing material. Tows according to the present invention
are useful, for example, for making metal matrix wires.

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CERAMIC OXIDE FIBERS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/755,690, filed Dec. 30, 2005, the disclosure of which is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The present invention related to ceramic oxide fibers, more particularly to ceramic oxide fibers with sizing material.

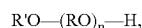
BACKGROUND

[0003] In general, substantially continuous ceramic oxide fibers are known. Examples include polycrystalline alumina fibers such those marketed by the 3M Company, St. Paul, Minn., under the trade designation "NEXTEL 610", aluminosilicate fibers such as those marketed by the 3M Company under the trade designations "NEXTEL 440", "NEXTEL 550", and "NEXTEL 720", and aluminoborosilicate fibers such as those marketed by the 3M Company under the trade designation "NEXTEL 312". These continuous fibers are incorporated into various metal matrix composites (e.g. aluminum and titanium) and polymer matrix composites (e.g. epoxy) to reinforce and strengthen these composites.

[0004] It is desirable to maintain the strength of the composites. The composite strengths are increased by having continuous fibers with as few discontinuities as possible. One source of discontinuities comes when the continuous fiber is unwound from a spool and the fiber breaks or sheds, commonly called "strip back." It is desirable to eliminate, minimize, or at least reduce these discontinuities produced during the unwind process thus allowing for the production of increased strength metal and polymer matrix composites.

SUMMARY

[0005] In one aspect, the present invention provides a tow of substantially continuous refractory (i.e., maintains its integrity or usefulness at temperatures in a range of 820° C. to 1400° C.) ceramic oxide fibers, wherein each ceramic oxide fiber has an outer surface, and wherein at least a portion of the outer surfaces of at least some of the ceramic oxide fibers have a sizing material therein. The sizing material comprises a composition represented by the formula:



wherein R' is selected from C_xH_{2x+1} , wherein x is 1-8 or —H; R is selected from the group consisting of $-(C_yH_{2y})-$ (which may be linear or branched), wherein y is 1-4, and $-(CH_2O-(CH_2)_m-$, wherein m=2-5; and wherein n is chosen such that the number average molecular weight is in a range from 500 g/mole to 7,000,000 g/mole. Typically, the number average molecular weight is in a range from 500 g/mole to 3,000,000 g/mole (in some embodiments, in a range from 500 g/mole to 600,000 g/mole, 500 g/mole to 400,000 g/mole, 500 g/mole to 300,000 g/mole, or even 4,000 g/mole to 40,000 g/mole). Typically the sizing material provides an add-on weight in a range from 0.5 to 10 percent by weight.

[0006] "Continuous fiber" refers to fiber having a length that is at least 30 meters. In some embodiments, the refractory fibers are crystalline (i.e., exhibits a discernible X-ray

powder diffraction pattern). In some embodiments, the fiber is at least 50 (in some embodiments, at least 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even 100) percent by weight crystalline. In some embodiments, the refractory ceramic oxide fibers (including crystalline ceramic oxide fibers) comprise at least one of (a) at least 40 (in some embodiments, at least 50, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even 100) percent by weight Al_2O_3 , based on the total oxide content of each respective fiber, or (b) not more than 40 (in some embodiments, not more than 35, 30, 25, 20, 15, 10, 5, 4, 3, 2, 1, 0.5, 0.1, or even zero) percent by weight collectively SiO_2 , Bi_2O_3 , B_2O_3 , P_2O_5 , GeO_2 , TeO_2 , As_2O_3 , and V_2O_5 , based on the total oxide content of each respective fiber.

[0007] The sizing material has been observed to provide lubricity and to protect the fiber strands during handling. For some uses of the fiber, for example, as reinforcement in a metal matrix composite, the sizing is typically removed during processing prior to applying metal to the fiber. The sizing may be removed, for example, by burning the sizing away from the fibers.

DESCRIPTION

[0008] Examples of suitable refractory ceramic oxide fibers include alumina fibers, aluminosilicate fibers, aluminoborate fibers, aluminoborosilicate fibers, zirconia-silica fibers, and combinations thereof. Examples of suitable crystalline refractory ceramic oxide fibers include alumina fibers, aluminosilicate fibers, aluminoborate fibers, aluminoborosilicate fibers, zirconia-silica fibers, and combinations thereof. Examples of suitable non-crystalline, refractory ceramic oxide fibers include aluminoborosilicate fibers, zirconia-silica fibers, and combinations thereof. In some embodiments, it is desirable for the fibers to comprise at least 40 (in some embodiments, at least 50, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or even 100) percent by volume Al_2O_3 , based on the total volume of the fiber. In some embodiments, it is desirable for the fibers to comprise in a range from 40 to 70 (in some embodiments, in a range from 55 to 70, or even 55 to 65) percent by volume Al_2O_3 , based on the total volume of the fiber.

[0009] The partially crystalline fibers can comprise a mixture of crystalline ceramic and amorphous phases (i.e., a fiber may contain both crystalline ceramic and amorphous phases). Typically, the continuous ceramic fibers have an average fiber diameter of at least about 5 micrometers, more typically, in a range from about 5 micrometers to about 20 micrometers; in some embodiments, in a range from about 5 micrometers to about 15 micrometers.

[0010] Alumina fibers are described, for example, in U.S. Pat. Nos. 4,954,462 (Wood et al.) and 5,185,299 (Wood et al.). In some embodiments, the alumina fibers are polycrystalline alpha alumina fibers, and comprise, on a theoretical oxide basis, greater than 99 percent by weight Al_2O_3 and 0.2-0.5 percent by weight SiO_2 , based on the total weight of the alumina fibers. In another aspect, some desirable polycrystalline, alpha alumina fibers comprise alpha alumina having an average grain size of less than 1 micrometer (or even, in some embodiments, less than 0.5 micrometer). In another aspect, in some embodiments, polycrystalline, alpha alumina fibers have an average tensile strength of at least 1.6 GPa (in some embodiments, at least 2.1 GPa, or even, at

least 2.8 GPa), as determined according to the tensile strength test described in U.S. Pat. No. 6,460,597 (McCullough et al.). Exemplary alpha alumina fibers are marketed under the trade designation "NEXTEL 610" by 3M Company, St. Paul, Minn.

[0011] Aluminosilicate fibers are described, for example, in U.S. Pat. No. 4,047,965 (Karst et al). Exemplary aluminosilicate fibers are marketed under the trade designations "NEXTEL 440", "NEXTEL 550", and "NEXTEL 720" by 3M Company of St. Paul, Minn.

[0012] Aluminoborate and aluminoborosilicate fibers are described, for example, in U.S. Pat. No. 3,795,524 (Sowman). Exemplary aluminoborosilicate fibers are marketed under the trade designation "NEXTEL 312" by 3M Company.

[0013] Zirconia-silica fibers as described, for example, in U.S. Pat. No. 3,709,706 (Sowman).

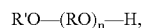
[0014] Tows are known in the fiber art and typically include a plurality of (individual) generally untwisted fibers (typically at least 100 fibers, more typically at least 400 fibers). In some embodiments, tows comprise at least 780 individual fibers per tow, and in some cases, at least 2600 individual fibers per tow, or at least 5200 individual fibers per tow. Tows of various ceramic fibers are available in a variety of lengths, including 300 meters, 500 meters, 750 meters, 1000 meters, 1500 meters, and longer. The fibers may have a cross-sectional shape that is circular, elliptical, or dogbone.

[0015] A tow(s) according to the present invention can be made by a method comprising:

[0016] providing a tow of substantially continuous ceramic oxide fibers, wherein each ceramic oxide fiber has an outer surface;

[0017] coating at least a portion of the outer surfaces of at least some of the ceramic oxide fibers with an aqueous-based sizing material; and

[0018] removing at least a portion of the water. The aqueous-based sizing material comprises a composition represented by formula:



wherein R' is selected from C_xH_{2x+1} , wherein x is 1-8 or -H; R is selected from the group consisting of $-(C_yH_{2y})-$, wherein y is 1-4, and $-CH_2-O-(CH_2)_m-$, wherein m=2-5; and wherein n is chosen such that the number average molecular weight is in range from 500 g/mole to 7,000,000 g/mole. Typically, the number average molecular weight is in a range from 500 g/mole to 3,000,000 g/mole (in some embodiments, in a range from 500 g/mole to 600,000 g/mole, 500 to 400,000 g/mole, 500 g/mole to 300,000 g/mole, or even 4,000 g/mole to 40,000 g/mole).

[0019] Suitable sizing materials include poly(tetramethylene oxide) (available, for example, from Invista, Wichita, Kans., under the trade designation "TERATHANE 2900" (number average molecular weight 2,900 g/mole)), polyethylene glycol (available, for example, from Clariant GmbH Functional Chemicals Division, Frankfurt, Germany, under the trade designation "POLYGLYKOL 35000" (number average molecular weight 35,000 g/mole) "POLYGLYKOL

20000" (number average molecular weight 20,000 g/mole), "POLYGLYKOL 4000S" (number average molecular weight 4000 g/mole), "POLYGLYKOL 8000S" (number average molecular weight 8000 g/mole), "POLYGLYKOL 1500S" (number average molecular weight 1500 g/mole)), and high number average molecular weight polyethylene oxide materials (available, for example, from Dow Chemical, Midland, Mich., under the trade designation "POLYOX WSR N-3000" (number average molecular weight 400,000 g/mole), "POLYOX WSR N-750" (number average molecular weight 300,000 g/mole) and "POLYOX WSR-301" (number average molecular weight 4,000,000 g/mole).

[0020] Water soluble sizing materials such as poly(ethylene glycols) may be dissolved in water to provide the aqueous-based sizing material. The concentration of water soluble sizing materials in the aqueous-based sizing material can be chosen as desired. Typically, such aqueous-based sizing materials are made by combining the water soluble sizing material and water to provide an aqueous-based sizing material comprising, by weight, in a range from 1 to 30 percent; in some embodiments, in a range from 1 to 10 percent water soluble sizing materials.

[0021] When using materials that are not soluble in water (e.g., poly(tetramethylene oxide)), the aqueous-based sizing material is emulsified. Such emulsions can be made with the use of surfactants. Typically, the amount of surfactant used to make the emulsion is in a range from 0.5 to 10% percent by weight of the material to be emulsified, although amounts of surfactant outside of this range may also be useful. Typically, the emulsion is in a range from 5 to 50 percent by weight solids. If the percent solids of the emulsion is higher than desired, it can be diluted with water.

[0022] In general sizing materials have been observed in the art to provide (a) sufficient strength to bind the fibers in the tow together into a cohesive bundle, (b) good lubricating/release characteristics so that the fibers/tows do not stick to equipment and thread guides, and have lubrication to reduce friction and adherence to surfaces that contact the tow during handling, and (c) ability to be rapidly oxidized without leaving residue (e.g., carbon-containing residue) on the fiber at relatively low or moderate temperatures, (e.g., 700° C.). The later is particularly desirable in embodiments of metal matrix wire making process, wherein the sizing material is typically easily removed in a relatively short period of time (e.g., less than 30 seconds) by heating the tows at the relatively low or moderate temperatures. Removal of the sizing material is enhanced by pumping an oxidizing gas (e.g., air) into the region where the sizing material is being oxidized. Although the desired flow rates of the oxidizing gas will depend on the particular circumstances (e.g., the particular sizing material, the amount of sizing material, the fiber speed, the temperature, the length of the hot zone, etc.), exemplary flow rates include flow rates in a range from about 5 liters/min. to about 10 liters/min.

[0023] Further, the sizing material specified for the present invention can be effectively applied to fiber (e.g., fiber at a temperature in a range of about 15° C.-200° C.), including applying the sizing material to fiber as it exits the sintering furnace.

[0024] Tows according to the present invention are useful, for example, for making metal matrix composite wires. Exemplary metal matrix materials include aluminum, zinc,

tin, magnesium, and alloys thereof (e.g., an alloy of aluminum and copper). Techniques for making metal matrix composite wires are known in the art, and include those discussed, for example, in U.S. Pat. Nos. 5,501,906 (Deve), 6,180,232 (McCullough et al.), 6,245,425 (McCullough et al.), 6,336,495 (McCullough et al.), 6,544,645 (McCullough et al.), 6,447,927 (McCullough et al.), 6,460,597 (McCullough et al.), 6,329,056 (Deve et al.), 6,344,270 (McCullough et al.), 6,485,796 (Carpenter et al.), 6,559,385 (Johnson et al.), 6,796,365 (McCullough et al.), 6,723,451 (McCullough et al.), 6,692,842 (McCullough et al.), 6,913,838 (McCullough et al.), 7,093,416 (Johnson et al.), and 7,131,308 (McCullough et al.); U.S. publication No. 2005/0181228-A1; U.S. application having Ser. No. 10/403,643, filed Mar. 31, 2003, U.S. application having Ser. No. 10/870,263, filed Jun. 17, 2004, and U.S. application having Ser. No. 10/870,401, filed Jun. 17, 2004, the disclosures of which are incorporated herein by reference for their teachings on making and using metal matrix composite wires.

[0025] Embodiments of metal matrix composite wires made from sized fibers according to the present invention have been observed to be stronger (e.g., about 2-8%) as compared to the metal matrix composite wires made fibers not including the sizing material utilized in the present invention (including fibers sized with other sizing materials).

[0026] Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Example 1

[0027] 52.2 kg (115 lbs.) of solid poly(tetramethylene oxide) (2900 g/mole number average molecular weight; obtained from INVISTA, Wichita, Kans., under the trade designation "TERATHANE 2900") was melted by placing it in an oven heated to 60° C. (140° F.) overnight. A 284 liter (75 gallon) glass-lined water-jacketed receiver, fitted with an agitator, was brought to 60° C. (140° F.). The agitator was set at 80 rpm, and the reactor charged with the molten poly(tetramethylene oxide) ("TERATHANE 2900"). 52.2 kg (115 lbs.) of ethyl acetate (obtained from Sigma-Aldrich, Milwaukee, Wis.) was then added to the reactor, followed by 8.7 kg (19.1 lbs.) of octadecylmethyl(polyoxyethylene[15]) ammonium chloride (obtained from Akzo Nobel, Chicago, Ill., under the trade designation "ETHOQUAD 18/25").

[0028] A second 284 liter (75 gallon) glass-lined water-jacketed reactor, fitted with an agitator (80 rpm) was brought to 60° C. (140° F.). 114 kg (253 lbs.) of de-ionized water; filtered through a 0.2 micron filter (obtained from C.C. Day Co., Minneapolis, Minn.; part No. 25-10110-002-01-WG), was added to the reactor. The agitator speed was increased to 100 rpm. Once the temperature of both the reactor and the receiver were at 60° C. (140° F.), nitrogen pressure on the receiver was increased to allow the contents from the first reactor to flow into the second reactor.

[0029] The water inlet connection of a two stage homogenizer (type 70-M-310-TBS; obtained from Manton-Gaulin

Manufacturing Co., Everett, Mass.; flushed with de-ionized water) was attached to the inlet port of the homogenizer with a tube and a 0.2 micron filter (obtained from C.C. Day Co.; part No. 25-10110-002-01-WG). A 25 micrometer filter cartridge (obtained from C.C. Day Co.; part No. SWF-25-RYA10T) was attached between the outlet of the reactor and the inlet connection of the homogenizer. The operating pressure of the homogenizer was set at 20.7 MPa (3000 psig), and the mixture pumped through at 20.7 MPa (3000 psig). Once the output from the homogenizer was a bluish-white emulsion with no solids, the output was directed into 208 liter (55 gallon) drums with polyethylene liner.

[0030] The bluish-white emulsion was run through the homogenizer a second time, and the output again directed into 208 liter (55 gallon) drums with polyethylene liners. The first reactor was fitted with a condensate decanter, flushed and cleaned with de-ionized water before the bluish-white emulsion was charged into the (clean) reactor. The agitator was brought to 60 rpm, and the jacket temperature set to 38° C. (100° F.). The reactor was then closed and a vacuum (8 kPa (60 mm Hg)) drawn on the contents. As ethyl acetate distillate collected in the decanter, the vacuum was slowly increased to (5.3 kPa (40 mm Hg)), to minimize excessive foaming. When 45.4 kg (100 lbs.) of ethyl acetate has been collected, the distillation was terminated, the reactor cooled to 21° C. (70° F.), and the resulting emulsion drained through a 25 micrometer cartridge filter (obtained from C.C. Day Co.; part No. SWF-25-RYA10T), into 19 liter (5 gallon) polyethylene-lined pails and covered.

[0031] The resulting emulsion was coated onto tows of alpha alumina fibers (10,000 denier; marketed by the 3M Company, St. Paul, Minn., under the trade designation "NEXTEL CERAMIC OXIDE FIBER 610") using a coating station according to the following procedure. The "TERATHANE 2900" emulsion, as described above, was diluted with deionized water to a 5% "TERATHANE 2900" emulsion, and placed into the sizing tray of the coating station. The sizing roll picks up the emulsion by immersion in the coating tray. The sizing was coated onto one fiber tow by passing the tow over the sizing roll, at a rate of 34.7 m/min. (114 ft./min.). The speed of the sizing application roll was set to provide 1.5% sizing net coating weight. The coated fiber tow was wrapped around drying cans (15 cm (6 inch) diameter chrome-coated steel rolls heated to 100° C.) twelve times and then wound onto cardboard cylinders.

* The fiber used was unsized prior to application of the emulsion. The fiber marketed by 3M typically is sold with a sizing thereon. Such sizing can typically be removed by heating the fiber to at least 700° C. for 5 minutes.

[0032] The amount of sizing applied to the fiber tow was determined by weighing a one meter (3 ft) piece of sized tow ($w_{initial}$), placing the piece of sized tow in a furnace at 700° C. for 5 minutes, removing the sample from the furnace, allowing the to cool to room temperature, and then reweighing the sample (w_{final}). The weight percent sizing applied (S_w) was calculated using the following formula:

$$S_w = \frac{(w_{initial} - w_{final})}{w_{initial}} \times 100$$

[0033] The add-on weight of the dried sizing material was about 2% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 2

[0034] A 4 liter (1 gallon) glass jar was charged with 2858 grams of de-ionized water. An overhead mixer fitted with a Cowl's blade mixer was inserted into the glass jar, brought to 500 rpms, and 150 grams of polyethylene glycol (300,000 g/mole number average molecular weight; obtained from Dow Chemical, Midland Mich., under the trade designation "POLYOX WSR N-750") slowly added (over about 30 minutes) at the vortex created by the Cowl's blade. The resulting mixture was placed on a platform shaker table (obtained from New Brunswick Scientific Co. Inc., Edison, N.J., under the trade designation "INNOVA 2000") for about 60 hours.

[0035] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 3

[0036] Example 3 was prepared as described for Example 2, except 3 grams of polyethylene glycol (1500 g/mole number average molecular weight; obtained from Sigma-Aldrich, Milwaukee, Wis., under the trade designation "PEG 1500") was added to the deionized water before the polyethylene glycol.

[0037] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1.5% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 4

[0038] Example 4 was prepared as described for Example 2, except 150 grams of polyethylene glycol (20,000 g/mole number average molecular weight; obtained from Sigma-Aldrich, under the trade designation "PEG 20,000") was substituted for the polyethylene glycol. The resulting material was a clear solution.

[0039] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 5

[0040] A 3.8 liter (one gallon) glass jar was charged with 2850 grams of de-ionized water. An overhead mixer fitted with a Cowl's blade mixer was inserted into the glass jar, brought to 500 rpms, and 150 grams of polyethylene glycol (35,000 g/mole number average molecular weight; obtained from Clariant Corporation, Mount Holly, N.C. under the trade designation "POLYGLYKOL 35000") slowly added (over about 10 minutes) at the vortex created by the Cowl's blade. The resulting material was a clear, colorless solution.

[0041] The resulting solution was diluted and coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 6

[0042] A 6 liter stainless steel beaker was charged with 2970 grams of de-ionized water and a mixer (Model # ME100L obtained from Charles Ross & Son Co. Hauppauge, N.Y.; under the trade designation "ROSS MIXER EMULSIFIER") was inserted into the beaker. The mixer was brought to 5000 rpm, and 30 grams of polyethylene glycol (4,000,000 g/mole number average molecular weight; obtained from Dow Chemical under the trade designation "POLYOX WSR-301") was slowly added (over about 15 minutes) to the water. The resulting mixture was placed on a shaker table (see Example 2; at 125 rpm) for 12 hours.

[0043] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1.5% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 7

[0044] A 6 liter stainless steel beaker was charged with 2985 grams of de-ionized water. An overhead mixer fitted with a Cowl's blade mixer was inserted into the glass jar, brought to 500 rpms, and 15 grams of polyethylene glycol (7,000,000 g/mole number average molecular weight; obtained from Dow Chemical under the trade designation "POLYOX WSR-303") slowly added (over about 30 minutes) to the water. The resulting mixture was placed on a shaker table (see Example 2; at 125 rpm) for 12 hours.

[0045] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 2% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 8

[0046] A 6 liter stainless steel beaker was charged with 2850 grams of de-ionized water, and a mixer ("ROSS MIXER EMULSIFIER") fitted with a Ross screen head was inserted into the beaker. The mixer was brought to 5000 rpm, and the water heated to about 60° C., 30 grams of polyethylene glycol ("POLYOX WSR N-750") was slowly added (over about 15 minutes) to the water. The resulting mixture was placed on a conventional roller table (at about 40 rpm) for 12 hours, yielding a cloudy solution.

[0047] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1.3% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 9

[0048] A 6 liter stainless steel beaker was charged with 2850 grams of de-ionized water and a mixer ("ROSS MIXER EMULSIFIER") fitted with a Ross disperser blade was inserted into the beaker. The mixer was brought to 5000 rpm, and the 150 grams of polyethylene glycol (400,000 number average MW; obtained from Dow Chemical under the trade designation "POLYOX WSR N-3000") was slowly added (over about 30 minutes) to the water. This resulted in a clear solution.

[0049] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1.5% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 10

[0050] Example 10 was prepared as described for Example 3, except polyethylene glycol (4000 g/mole number average molecular weight; obtained from Clariant Corporation under the trade designation "POLYGLYKOL 4000S") was added to the deionized water instead of the "PEG 1500" polyethylene glycol.

[0051] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 1.3% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 11

[0052] Example 11 was prepared as described for Example 10, except polyethylene glycol (8000 g/mole number average molecular weight; obtained from Clariant Corporation under the trade designation "POLYGLYKOL 8000S") was added to the deionized water instead of the "POLYGLYKOL 4000S" polyethylene glycol.

[0053] The resulting solution was coated onto tows of alumina fibers as described in Example 1. The add-on weight of the dried sizing material was about 2% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

Example 12

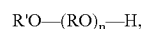
[0054] Example 12 was prepared as described for Example 2, except 147 grams "POLYOX WSR N-750" and 3.02 grams of "PEG-1500" was added to the deionized water instead of 150 grams of the "POLYOX WSR N-750" polyethylene glycol. The add-on weight of the dried sizing material was about 1.2% by weight. The sizing material was visually observed to have cleanly burned-off the fibers.

[0055] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. A tow of substantially continuous ceramic oxide fibers, wherein each ceramic oxide fiber has an outer surface, wherein at least a portion of the outer surfaces of at least some of the ceramic oxide fibers have a sizing material

therein, and wherein the sizing material comprises a composition represented by the formula:



wherein:

R' is selected from C_xH_{2x+1} , wherein x is 1-8 or —H;

R is selected from the group consisting of $-(C_yH_{2y})-$, wherein y is 1-4, and $-CH_2-O-(CH_2)_m-$, wherein m=2-5; and

n is chosen such that the number average molecular weight is in a range from 500 g/mole to 7,000,000 g/mole.

2. The tow according to claim 1, wherein the substantially continuous ceramic oxide fibers are crystalline.

3. The tow according to claim 1, wherein the substantially continuous ceramic oxide fibers are selected from the group consisting of crystalline alumina fibers, crystalline aluminosilicate fibers, crystalline aluminoborosilicate fibers, and combinations thereof.

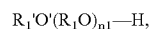
4. The tow according to claim 1, wherein n is chosen such that the number average molecular weight is in a range from 500 g/mole to 3,000,000 g/mole.

5. The tow according to claim 1, wherein n is chosen such that the number average molecular weight is in a range from 500 g/mole to 400,000 g/mole.

6. A method of providing the tow of substantially continuous ceramic oxide fibers according to claim 1, the method comprising:

providing a tow of substantially continuous ceramic oxide fibers, wherein each ceramic oxide fiber has an outer surface;

coating at least a portion of the outer surfaces of at least some of the ceramic oxide fibers with an aqueous-based sizing material, wherein the sizing material comprises a composition represented by formula:



wherein:

R₁' is selected from $C_{x1}H_{2x1+1}$, wherein x₁ is 1-8 or —H;

R₁ is selected from the group consisting of $-(C_{y1}H_{2y1})-$, wherein y₁ is 1-4, and $-CH_2-O-(CH_2)_{m1}-$, wherein m₁=2-5; and wherein n is chosen such that the number average molecular weight is in a range from 500 g/mole to 7,000,000 g/mole; and

removing at least a portion of the water.

7. The method according to claim 6, wherein the aqueous-based sizing material is a solution.

8. The method according to claim 6, wherein the aqueous-based sizing material is an emulsion.

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