Kirk-Othmer Encyclopedia of Chemical Technology.

REFRACTORY FIBERS

Fibrous materials may be naturally occurring or synthetically manufactured by thermal or chemical processes (Fig. 1) (see Fibers, survey). Refractory fibers are generally used in industrial applications at temperatures between 1000°C and 2800°C. These fibers may be oxides or nonoxides, vitreous or polycrystalline, and may be produced as whiskers, continuous filaments, or loose wool products.

Fiber chemistry determines whether the material is an oxide or nonoxide and can also influence its vitreous or polycrystalline physical form. Refractory fibers generally have diameters ranging from submicrometer to 10 μm, and lengths, as manufactured, may range from millimeters to continuous filaments.

Oxide fibers are manufactured by thermal or chemical processes into a loose wool mat, which can then be fabricated into a flexible blanket; combined with binders and formed into boards, felts, and rigid shapes; or fabricated into ropes, textiles and papers. The excellent thermal properties of these products make them invaluable for high temperature industrial applications.

Nonoxide fibers, such as carbides, nitrides, and carbons, are produced by high temperature chemical processes that often result in fiber lengths shorter than those of oxide fibers. Mechanical properties such as high elastic modulus and tensile strength of these materials make them excellent as reinforcements for plastics, glass, metals, and ceramics. Because these products oxidize at high temperatures, they are primarily suited for use in vacuum or inert atmospheres, but may also be used for relatively short exposures in oxidizing atmospheres above 1000°C.

1. Properties

Refractory fibers are most often used in applications above 1000°C. Table 1 shows the maximum long-term use temperatures in both oxidizing and nonoxidizing atmospheres. For short exposures, however, some of these fibers can be used with little degradation at temperatures within 100°C of their melting points.

The most important properties of refractory fibers are thermal conductivity, resistance to thermal and physical degradation at high temperatures, tensile strength, and elastic modulus. Thermal conductivity is affected by the material's bulk density, its fiber diameter, the amount of unfiberized material in the product, and the mean temperature of the insulation. Products fabricated from fine fibers with few unfiberized additions have the lowest thermal conductivities at high temperatures. A plot of thermal conductivity versus mean temperature for three oxide fibers having equal bulk densities is shown in Figure 2.

The effect of bulk density on thermal conductivity for silica and aluminosilicate fibers is shown in Figure 3. At relatively low densities, solid conduction of heat is negligible when considering the total heat transfer. This is because radiation is responsible for the majority of the heat passing through the insulation. Convection and gas conduction are also factors that affect heat transfer, but these are minor influences at the higher use temperatures. For example, at 1260°C, over 80% of the heat transfer is the result of radiation. ASTM C201 and ASTM C177 are the standard test procedures for measuring the thermal conductivity of refractory fiber materials.

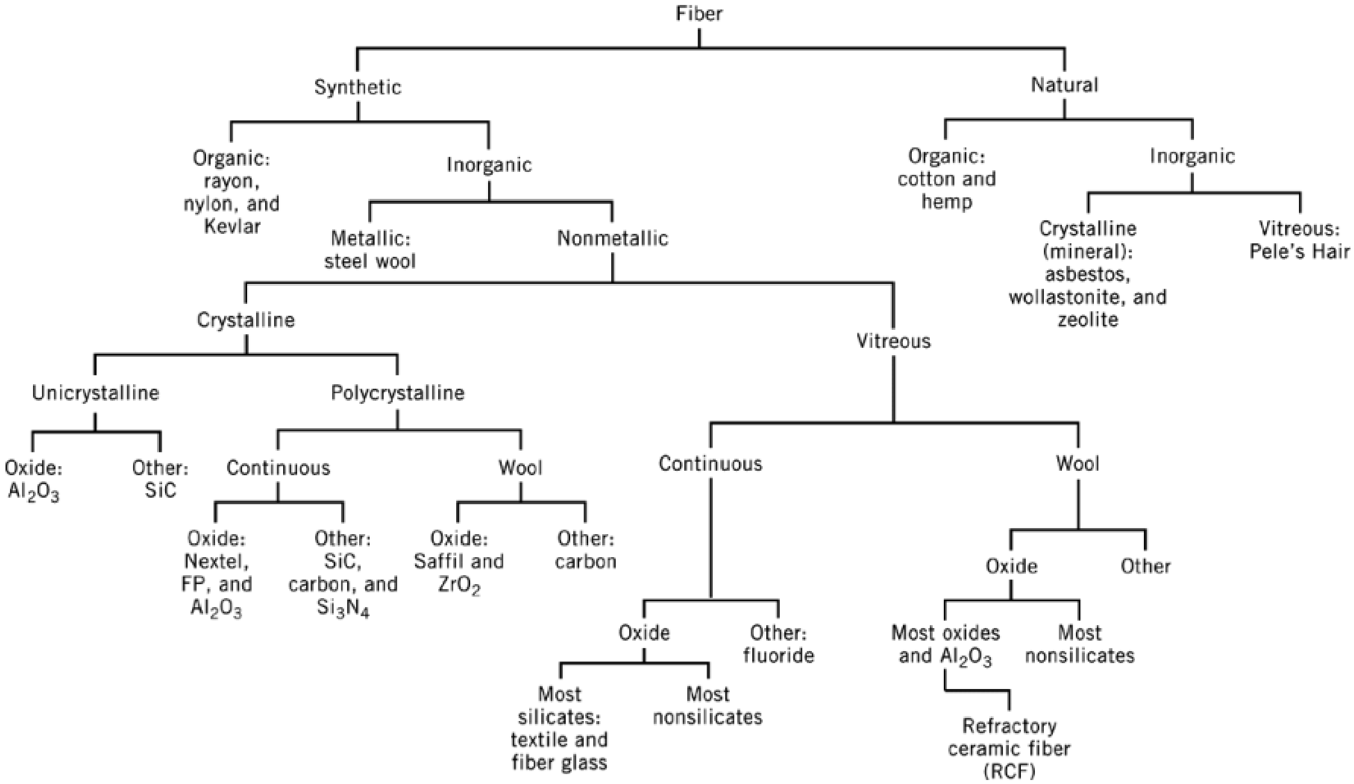

Fig. 1. Fiber classification tree.

For reinforcement, room temperature tensile strength and Young's modulus (stress–strain ratio) are both important. Typical values for refractory fibers are shown in Table 2.

Heat treatment of vitreous refractory fibers often results in crystallization of the fiber (1). The rate of crystallization (qv), sometimes called devitrification, depends on temperature and time. Shrinkage and degradation of mechanical strength are attributable to this crystallization. Sintering, the bonding together of refractory fibers at temperatures below their softening points, is also responsible for shrinkage. At fiber contact points, solid-state diffusion of molecules joins the fibers together and transforms the previously flexible structure into a rigid mass. Figure 4 shows a scanning electron micrograph of alumina–silica–chromia fibers after exposure to a temperature of 1426°C for 120 h. The formation of mullite crystals in the vitreous fiber and the sintering at the fiber intersections are both visible. The diffusion of oxides in the fibers toward these contact points produces a shortening effect, which ultimately contributes to the overall shrinkage of the product. The property of linear shrinkage is an important design consideration for industrial furnaces and other high temperature applications.

2. Nonoxide Refractory Fibers

The most important nonoxide refractory fiber is silicon carbide. It was first produced as fibers or whiskers by a thermal/chemical process in which one part silica was mixed with three parts carbon monoxide in an inert carrier gas at temperatures of 1300–1500°C. Silicon carbide fibers form in the cooler parts of the reactor

Table 1. Maximum Use Temperatures of Refractory Fibers

Fiber type	Name	CAS Registry Number	Mp, °C	Use temperature, °C, max	
				[a]	[b]
Al_2O_3	aluminum oxide	[1344-28-1]	2040	1540	1600
ZrO_2	zirconium oxide	[1314-23-4]	2650	1650	1650
SiO_2	silica	[7631-86-9]	1660	1060	1060
Al_2O_3–SiO_2	aluminosilicate	[142844-00-6]	1760	1300	1300
Al_2O_3–SiO_2–Cr_2O_3	chromia alumino-silicate	[142844-00-6]	1760	1430	1430
Al_2O_3–SiO_2–ZrO_2	zirconia alumino-silicate	[142844-00-6]	1760	1430	1430
CaO–MgO–SiO_2	calcium–magnesium silicate		1425	1000	1000
C	carbon	[7440-44-0]	3650	400	2500
B	boron	[7440-42-8]	1260	560	1200
BN	boron nitride	[10043-11-5]	2980	700	1650
SiC	silicon carbide	[409-21-2]	2690	1550	1800
Si_3N_4	silicon nitride	[12033-89-5]	1900	1300	1800

[a] Oxidizing atmosphere
[b] Reducing atmosphere

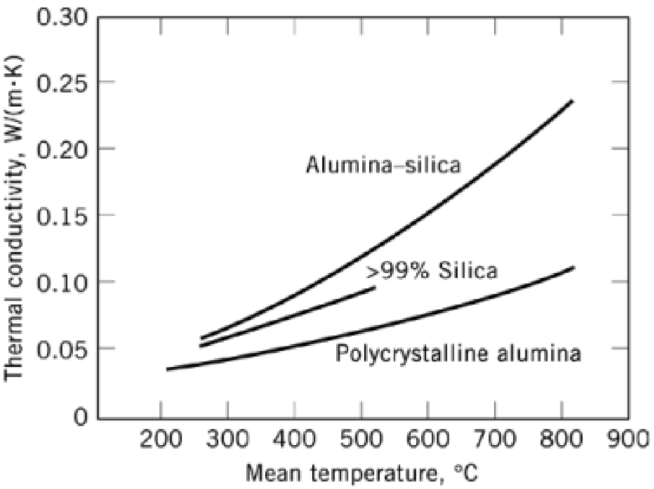

Fig. 2. Thermal conductivity of refractory fiber insulations with 96-mg/cm^3 density.

tube (2). A less complicated technique has been developed by Corning Glass Works, in which silica and carbon monoxide gases are first formed by heating a mixture of carbon and silica (molar ratio of 2:1) in a hydrogen fluoride or hydrogen chloride atmosphere at temperatures of 1300 to 1550°C (3). The fibers grow more quickly through this process, which can be operated continuously. The resulting fibers consist of β-silicon carbide crystals surrounded by a silica sheath that prevents oxidation. A more recent innovation is the production of silicon carbide fibers by the pyrolysis of rice hulls in an inert or ammonia atmosphere (4).

Since 1960, a number of processes have been developed to produce high quality silicon nitride fibers. These fibers are a by-product in the production of silicon nitride powder from the reaction of silicon metal in a nitrogen atmosphere at high temperatures. Fiber yields can be increased by first reducing silica to silicon monoxide and then to silicon metal before the reaction with nitrogen (5). R represents a reducing agent in the

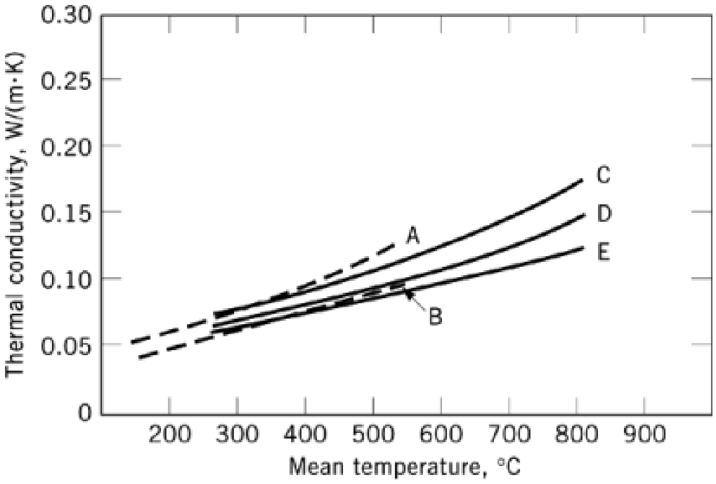

Fig. 3. Effect of density on thermal conductivity. A, 48-mg/cm^3 silica fiber; B, 96-mg/cm^3 silica fiber; C, 128-mg/cm^3 alumina–silica fiber; D, 192-mg/cm^3 alumina–silica fiber; E, 384-mg/cm^3 alumina–silica fiber.

Table 2. Mechanical Properties of Oxide and Nonoxide Fibers

Fiber type	Density, g/cm^3	Tensile strength, GPa[a]	Young's modulus, GPa[a]
SiO_2	2.19	5.9	72
Al_2O_3	3.15	2.1	170
ZrO_2	4.84	2.1	345
carbon	1.50	1.4	210
graphite[b]	1.66	1.8	700
BN	1.90	1.5	90
SiC[b]	3.21	2.0	480
Si_3N_4[b]	3.18	1.4	380

[a] To convert GPa to psi, multiply by 145,000.
[b] Single-crystal whiskers.

following equations.

$$SiO_2 + R \longrightarrow SiO + RO$$

$$3\ SiO + 3\ R + 2\ N_2 \longrightarrow RO + Si_3N_4$$

Any silicate that forms thermally and chemically stable residual compounds as its oxygen content is reduced provides a suitable source of silicon for this reaction. A typical process consists of alternating aluminum, silica, and graphite plates separated by 2–4-cm thick graphite spacers stacked in a graphite-lined alumina tube and heated to 1400°C for 12 h in a nitrogen atmosphere. After cooling for approximately 6 h the fibers are removed.

Boron nitride fibers are produced by nitriding boron filaments obtained during the chemical vapor deposition of boron on a heated tungsten wire (6, 7). The tungsten wire is first passed through a reactor operating at 1100–1300°C and containing boron trichloride in a hydrogen carrier gas. The boron trichloride is reduced

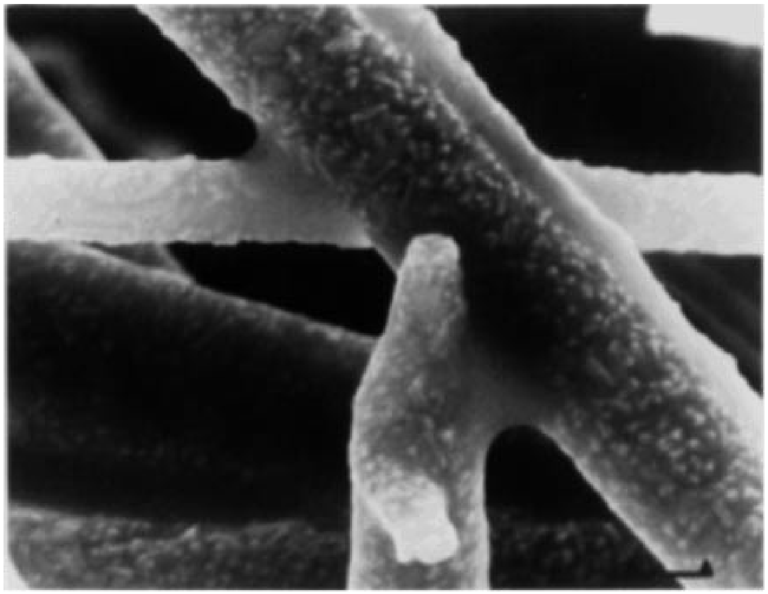

Fig. 4. Alumina–silica–chromia fiber after 120 h at 1426°C showing crystallization and sintering at contact points. Magnified $\times 5000$.

and boron is deposited onto the tungsten wire. To produce the boron nitride fiber, the boron filament is heated to 1000–1400°C in an ammonia atmosphere for approximately 6 h.

$$4\ \mathrm{B}\ (\mathrm{s}) + 3\ \mathrm{O_2} \longrightarrow 2\ \mathrm{B_2O_3}\ (\mathrm{l})$$

$$\mathrm{B_2O_3}\ (\mathrm{l}) + 2\ \mathrm{NH_3}\ (\mathrm{g}) \longrightarrow 2\ \mathrm{BN}\ (\mathrm{s}) + 3\ \mathrm{H_2O}\ (\mathrm{g})$$

Nonoxide fibers in continuous form, eg, carbon, graphite, and boron, are often used in filament winding and in the manufacture of high strength, high modulus fabrics. Lightweight, high strength pressure vessels can be made by impregnating these fibers with epoxy resins and winding them onto plaster mandrels. After curing the resin, the mandrel is dissolved, leaving a thin-walled vessel. Carbon fibers are also used in sporting goods such as golf club shafts and tennis rackets as well as aerospace applications such as radar-transparent military aircraft, light and durable communications satellites, jumbo jets, and high temperature-tolerant rocket motor nozzles. Drill stems used in the collection of lunar samples are a combination of boron cloth with an epoxy–graphite filament. Carbon fibers can be used in nonoxidizing processes at temperatures up to 1800°C. Approximately 6.8×10^6 kg of carbon fiber is produced globally. Prices range from \$22 to more than \$220/kg for the specialty grades (8) (see Carbon and graphite fibers).

Shorter, nonoxide filaments are primarily used as strength-enhancing reinforcements in resins, ceramics, and metals. These filaments have strengths of 1.4 to 20 GPa ($2 - 29 \times 10^5$ psi) and elastic moduli of 70 to 700 GPa ($1 - 10 \times 10^7$ psi). Silicon carbide whiskers (single-crystal fibers) are of special interest because they offer not only high strength and stiffness but also temperature resistance to 1800°C. Silicon carbide and silicon nitride fibers can be dispersed in a number of organic resins and then cast into shapes. These cast parts are used in high technology applications such as parts for specialty electronics, aircraft, and radomes. Boron nitride fibers are of particular value for the reinforcement of cast aluminum parts because the material can be wetted by molten aluminum. Silicon carbide and boron nitride are also used to reinforce gold and silver castings.

The growth and commercialization of the nonoxide fiber market parallels the high strength composite industry. If prices for nonoxide fibers with lengths of 2–10 cm reach the $10–20/kg range, a large potential market should develop.

3. Oxide Fibers

3.1. High Purity Silica Fibers

In 1942, the Owens-Corning Fiberglass Corporation developed a process for leaching and refiring E-glass fibers to give a $>99\%$ pure silica fiber (9). This fiber was widely used in jet engines toward the end of World War II. Shortly after the war, H. I. Thompson Co. began promoting silica insulating blankets for jet engines under the trade name Refrasil (10). In the 1950s, Micro-Quartz was developed by Glass Fibers, Inc. from a composition specifically designed for the leaching process (11).

In the 1990s, leached glass fibers having extremely fine diameters are produced using flame attenuation processing (see Glass) (12). A glass composed of 75 wt% SiO_2 and 25 wt% Na_2O is melted in a typical glass furnace at 1100°C. Filaments having diameters of 0.3 mm are drawn from orifices in the bottom of the furnace. These filaments are passed through a gas flame and attenuated to a diameter of approximately 1.5 μm. The loose fibers are then subjected to an acid leaching process to remove the Na_2O, thoroughly rinsed, and dried. The resulting fibers have a purity of $>99\%$ silica.

Several techniques for manufacturing fused silica fibers by rod-drawing were developed in the early 1960s by Engelhard Industries and others (13). Fused silica rods having diameters of 6 to 7 mm are formed from molten, high purity silica and mounted in groups on a motor-driven carriage. Rod diameters are then reduced to 2 mm by forcing the rods through graphite guides and over a vertically oriented oxyhydrogen burner operating at 1800°C. The relatively large processed fibers then pass through a second graphite block where they are attenuated by an axial oxyhydrogen flame before being collected on a rotating drum. This process produces fibers that have diameters between 4 and 10 μm and silica contents of 99.95% (14). High thermal efficiency insulating felts having very low bulk densities produced by rod-drawing are essentially free of unfiberized material and can be used not only for jet engine insulation but also for space vehicles (see Ablative materials). High purity silica fibers (Q Fiber) are used for the tiles of the reusable thermal protection system on the space shuttle.

In addition to aerospace uses, silica fibers can be twisted into sewing threads and yarns for weaving into fabrics. These fabrics are used extensively for heat-resistant clothing, flame curtains for furnace openings, thermocouple protection, and electrical insulation. The cloth can also be used to encapsulate other fibers to produce flexible sheets.

3.2. Chemically Produced Oxide Fibers

Refractory fibers from oxides of alumina or zirconia are difficult to manufacture by conventional melt technologies because of high melting points and low viscosities (see Ceramics). In 1969, Union Carbide began to market the first 1650°C zirconia refractory fiber manufactured by a chemical precursor process (15). The precursor in this process is an organic fiber containing extremely small crystallites of polymer chains held together in a matrix of amorphous polymer. When immersed in a solvent, such as water, the fiber swells, expanding the spaces between the crystallites. Although a number of organic fibers, eg, wool, cotton, and cellulose acetate, have this swelling characteristic, rayon is preferred because of its structural uniformity and high purity. After an initial swelling and centrifugal dewatering, the rayon fiber is immersed in a 2-*M* aqueous solution of zirconyl chloride containing a small amount of yttrium salt. The excess solution is centrifuged, the fibers are dried, and the remaining fibrous material is fired at 400°C in an atmosphere containing <10 vol % oxygen. This treatment pyrolyzes the rayon to a carbonaceous residue. At the same time the zirconyl chloride is converted to microcrystalline zirconia fibers containing yttrium oxide for phase stabilization.

Another process for the manufacture of high temperature refractory fibers was developed by Imperial Chemical Industries (16). Both silica-stabilized alumina and calcia-stabilized zirconia have been manufactured by this sol–gel process. To produce an alumina fiber, a metallic salt such as aluminum oxychloride is mixed with a medium molecular weight polymer such as 2 wt % poly(vinyl alcohol). The solution is slowly evaporated in a rotary evaporator to achieve a viscosity of $80\ \mathrm{Pa{\cdot}s}$ (800 P) and then extruded into fibers through a spinnerette. The fibers are collected and fired at 800°C to decompose the organic component. The resulting fine-grained alumina fibers have a porosity of 5 to 10 vol % and diameters of 3 to 5 μm. Fibers' inherent porosity makes them good for filtration and for use as catalytic substrates. For refractory applications the fibers are fired to 1400–1500°C for thermal stabilization and densification. Zirconia fibers can be produced using the same technology and with zirconium oxychloride, zirconium acetate, and calcia as the raw materials.

The 3M Company manufactures a continuous polycrystalline alumina–silica–boria fiber (Nextel) by a sol process (17). Aluminum acetate is dissolved in water and mixed with an aqueous dispersion of colloidal silica and dimethylformamide. This mixture is concentrated in a Rotavapor flask and centrifuged. The viscous mixture is then extruded through spinnerettes at 100 kPa (1 atm); the filaments are collected on a conveyor and heat-treated at 870°C to convert them to metallic oxides. Further heating at 1000°C produces the 10-μm diameter aluminum borosilicate fibers, which are suitable for fabrication into textiles for use at temperatures up to 1427°C.

Although more expensive than melt fiberization, the sol processes offer advantages in fiber chemistry selection. In melt fiberization, viscosity and surface tension are greatly influenced by additions of small quantities metallic oxides. In the sol process, where viscosity can be controlled independently, any number of metal salts may be added without adverse effects. These salts can serve as grain growth inhibitors, sintering aids, phase stabilizers, or catalysts.

3.3. Aluminosilicate Fibers

Vitreous aluminosilicate fibers, more commonly known as refractory ceramic fibers (RCF), belong to a class of materials known as synthetic vitreous fibers. Fiber glass and mineral wool are also classified as synthetic vitreous fibers, and together represent 98% of this product group. RCFs were discovered in 1942 (18) but were not used commercially until 1953. Typical chemical and physical properties of these materials are shown in Table 3.

RCF is produced by melting a combination of alumina and silica in approximately equal proportions or by melting kaolin clay in an electric resistance furnace (19, 20). Trace ingredients, eg, zirconia, chromic oxide, and boria, may be added to enhance product properties (21). The molten mixture is formed into fiber either by blowing an air stream onto the molten material flowing from an orifice in the bottom of the furnace, or by directing the molten material onto a series of spinning wheels. The fibers are collected in a chamber as loose wool and are either packaged for future processing or converted into a blanket (mat) by a secondary needling/heat-treating process. As produced, RCF typically contains 50–65 wt % fiber, with the remainder being unfiberized materials called shot (Fig. 5). Some shot is removed and recycled in the standard manufacturing process but additional separation steps may be required for certain applications.

3.3.1. Applications

RCF is primarily used in industrial applications where high temperature resistance, light weight, low thermal conductivity, and low heat storage are required. The light weight of RCF is particularly advantageous. Thermal properties are enhanced by the material's low bulk density. Lower capital costs can be realized because fewer

Table 3. Typical Physical and Chemical Properties of Refractory Ceramic Fibers

Properties	Kaolin-based RCF	High purity RCF	RCF with zirconia	RCF with chromia	Poly-crystalline alumina
		Physical			
color	white	white	white	blue/green	white
maximum temperature rating, up to °C	1260	1316	1427	1427	1649
melting point, °C	1760	1760	1760	1760	1816
continuous use limit[a], up to °C	1093	1177	1316	1371	1538
specific gravity[b]	2.56	2.65	2.65	2.65	3.3
specific heat, $J/(kg{\cdot}K)$[c] at 982°C	1089	1089	1089	1089	1047
fiber tensile strength, MPa[d]	1035				2000
fiber tensile modulus, GPa[e]	84				296
		Chemical[f]			
alumina	45	46	35	43	96
silica	53	54	50	54	4
zirconia			15		
chromium oxide				3	
other	1–2	trace	trace	trace	

[a] This temperature is reported as a guide. Actual use limit depends on such factors as application, construction, fiber thermal stability, and anchoring system.

[b] ASTM C135.

[c] To convert $J/(kg{\cdot}K)$ to $Btu/(lb{\cdot}{}^{\circ}F)$, divide by 4187.

[d] To convert MPa to psi, multiply by 145.

[e] To convert GPa to psi, multiply by 145,000.

[f] Chemical analysis, nominal, % weight basis after firing.

structural furnace components are required. Compared to conventional hard refractories, installation times are reduced with these fibrous products. Low physical strength and chemical attack by ferrous metals and slags are disadvantages of RCF.

RCF is sold in a variety of forms, such as loose fiber, blanket, boards, modules, cloth, cements, putties, paper, coatings, felt, vacuum-formed shapes, rope, braid, tape, and textiles. The products are principally used for industrial applications as insulation in furnaces, heaters, kiln linings, furnace doors, metal launders, tank car insulation, and other uses up to 1400°C. RCF-consuming industries include ferrous and nonferrous metals, petrochemical, ceramic, glass, chemical, fertilizer, transportation, construction, and power generation/incineration. Some newer uses include commercial fire protection and applications in aerospace, eg, heat shields; and automotive, eg, catalytic converters, metal reinforcement, heat shields, brake pads, and airbags.

Oxide and nonoxide refractory fibers have become essential materials for use in modern high temperature industrial processes and advanced commercial applications. Future process improvements, cost reductions, and performance enhancements are expected to expand the uses and markets for these specialized fibrous materials.

3.3.2. Health and Safety Factors

Concern has been expressed that synthetic vitreous fibers may pose a health hazard when inhaled. Research is ongoing, but epidemiological evidence, as of 1996, does not demonstrate a causal relationship between exposure to refractory ceramic fibers and the development of respiratory ailments, including cancer, fibrosis, and parenchymal disease (22). State-of-the-art inhalation toxicology research undertaken at the Research and Consulting Company (Switzerland) laboratories indicated that at extremely high doses (200+ times maximum recommended exposure levels) RCF is an animal carcinogen, but that a critical dose level may exist below which neither fibrosis nor tumors occur. The results of the toxicology research are under review. The International

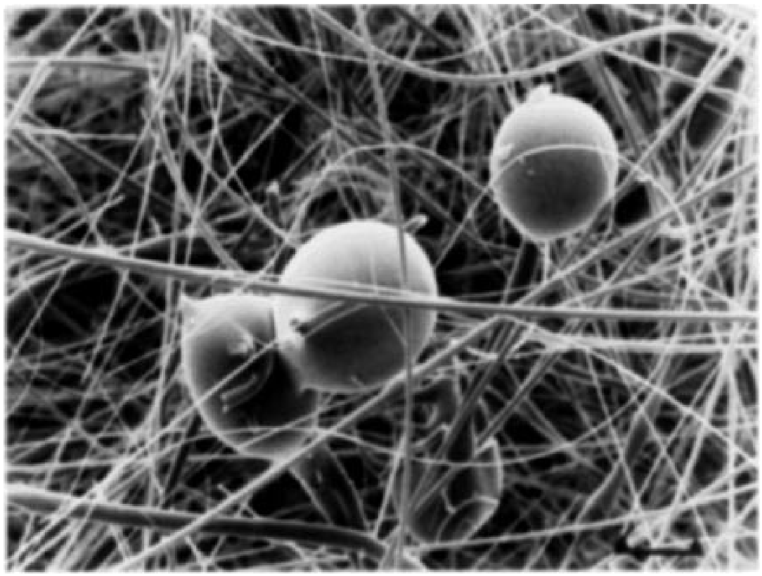

Fig. 5. Refractory fiber (1260°C) and unfiberized shot particles. Magnified ×1000.

Agency for Research on Cancer (IARC) has classified all respirable synthetic vitreous fibers as 2B, a possible carcinogen.

Silica and aluminosilicate fibers that have been exposed to temperatures above 1100°C undergo partial conversion to mullite and cristobalite (1). Cristobalite is a form of crystalline silica that can cause silicosis, a form of pneumoconiosis. IARC has determined that cristobalite should be classified as 2A, a probable carcinogen. The amount of cristobalite formed, the size of the crystals, and the nature of the vitreous matrix in which they are embedded are time- and temperature-dependent. Under normal use conditions, refractory ceramic fibers are exposed to a temperature gradient, thus only the hottest surfaces of the material may contain appreciable cristobalite. Manufacturers' Material Safety Data Sheets (MSDS) should be consulted prior to handling RCF materials.

BIBLIOGRAPHY

"Refractory Fibers" in *ECT* 2nd ed., Vol. 17, pp. 285–295, by T. R. Gould, Johns-Manville Corp.; in *ECT* 3rd ed., Vol. 20, pp. 65–77, by W. C. Miller, Manville Corp.

Cited Publications

1. L. Olds, W. Miller, and J. Pallo, *Am. Ceram. Soc. Bull.* **59**(7), 739 (1980).
2. U.S. Pat. 3,246,950 (Apr. 19, 1966), B. A. Gruber (to Corning Glass Works).
3. U.S. Pat. 3,371,995 (Mar. 5, 1968), W. W. Pultz (to Corning Glass Works).
4. U.S. Pat. 3,754,076 (Aug. 21, 1973), I. R. Cutler (to University of Utah).
5. U.S. Pat. 3,244,480 (Apr. 5, 1966), R. C. Johnson, J. K. Alley, and W. H. Warwick (to the United States of America).
6. U.S. Pat. 3,429,722 (July 12, 1965), J. Economy and R. V. Anderson (to Carborundum Co.).
7. U.S. Pat. 3,573,969 (Apr. 10, 1971), J. C. Millbrae and M. P. Gomez (to Lockheed Aircraft Corp.).
8. M. S. Reisch, *Chem. Eng. News*, **72**(48), 23 (Nov. 28, 1994).

9. U.S. Pat. 2,461,841 (Feb. 15, 1949), M. E. Nordberg (to Corning Glass Works).
10. *Chem. Eng. News* **25**(18), 1290 (1947).
11. U.S. Pat. 2,823,117 (Feb. 11, 1958), D. Labino (to Glass Fibers, Inc.).
12. U.S. Pat. 4,200,485 (Apr. 29, 1980), G. Price and W. Kielmeyer (to Johns-Manville Corp.).
13. U.S. Pat. 3,177,057 (Aug. 2, 1961), C. Potter and J. W. Lindenthal (to Engelhard Industries, Inc.).
14. Brit. Pat. 507,951 (June 23, 1939), (to W.C. Heraeus GmbH).
15. U.S. Pat. 3,385,915 (May 28, 1968), B. Hamling (to Union Carbide Corp.).
16. Brit. Pat. 1,360,197 (July 17, 1974), M. Morton, J. Birchall, and J. Cassidy (to Imperial Chemical Industries, Ltd.).
17. U.S. Pat. 3,760,049 (Sept. 18, 1973), A. Borer and G. P. Krogseng (to Minnesota Mining and Manufacturing Co.).
18. U.S. Pat. 2,467,889 (Apr. 19, 1949), I. Harter, C. L. Horton, Jr., and L. D. Christie, Jr. (to Babcock & Wilcox Co.).
19. U.S. Pat. 2,714,622 (Aug. 2, 1955), J. C. McMullen (to Carborundum Co.).
20. U.S. Pat. 3,066,504 (Dec. 4, 1962), F. J. Hartwig and F. H. Norton (to Babcock & Wilcox Co.).
21. U.S. Pat. 3,449,137 (June 10, 1969), W. Ekdahl (to Johns-Manville Corp.).
22. *The Epidemiology and Toxicology of Exposure to Refractory Ceramic Fibers*, RCF Coalition, Washington, D.C., Dec. 1993.

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