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Reinforcements—The Key to High Performance Composite Materials

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REINFORCEMENTS - THE KEY TO HIGH-PERFORMANCE COMPOSITE MATERIALS

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INTRODUCTION

High-temperature reinforcements are the key to high-performance composite materials. Such materials are the critical enabling technological issue in the design and development of 21st-century aerospace propulsion and power systems. The purpose of this section is to review some of the insights and findings developed on Japanese fibers and whiskers during the Japanese Technology Evaluation Center (JTEC) one-week visit to Japan and to examine these in light of current U.S. fiber technology.

Conventional materials are too heavy to provide effective structural members for future flight systems. The estimated cost of moving 1 pound to orbit is about $1000; cost per pound to the Moon is about $50,000; and cost per pound to Mars is about $500,000. Thus, the payoff for low-density, high-strength fibers and composites becomes clear. Figure 1 shows how high-performance composites could generally benefit any future high-speed civil transport aircraft. NO_x intrusion and noise must be overcome before such an aircraft can be considered feasible. Minimal environmental intrusion is contingent on combustors that can operate at extremely high temperatures and so must be constructed of, for example, ceramic matrix composites. Minimal airport noise is contingent on the exhaust nozzles. These will be very large (using conventional materials they could represent nearly half of engine weight). Such nozzles require high-temperature, lightweight intermetallic and ceramic composite structures. In addition, if such composites are used in future high-efficiency engines, lower engine weights will lead to very large reductions in aircraft structural weight. Some estimates approach a 40 percent structural weight reduction compared with conventional materials. These large weight savings could also be translated into more fuel capacity and thus substantial extension in range. This would make the Pacific rim a viable option for high-speed commercial flights.

The efficiency of the aircraft engines themselves is the final factor in commercial desirability. These engines will operate at extremely high temperatures for substantial fractions of their flight cycle. This means that in addition to the combustor and the nozzle, turbine blades, vanes, and disks and even the compressor blades and disks will be required to operate at temperatures substantially beyond those in current transport engines (fig. 2). High operating temperatures lead to requirements for high-temperature, high-strength fibers and composites that can resist thermal cycling, creep, and oxidizing environments.

Such applications help set high-temperature fiber property goals, as seen in figure 3. According to the rule of mixtures (a first approximation of composite properties based on the contributions of the volume fractions of the fiber and of the matrix), a 50-volume-percent composite of aluminum oxide fibers in a superalloy matrix could, because of its fiber density of only about 4 g/cm^3, lower the total density from 8 to 6 g/cm^3 and substantially lower rotational stresses as well as total component weight. More importantly, high strength and stiffness can raise the mechanical properties of a composite material beyond those achievable by today's superalloys and titanium alloys.

The issue of thermal expansion match between fiber and matrix is a key one. Large differences can result in a wide spectrum of dysfunctional situations ranging from matrix expansion away from the fibers with high temperature and thus minimal load transfer to severe thermal racheting, which can result in substantial distortion of the composite after repeated thermal cycles. Phase and microstructural stability are particularly important factors for commercial high-speed aircraft engines that must operate near maximum temperature for substantial fractions of their 16 000-hr plus life. Phase decomposition, such as the gamma to alpha transition that can occur in aluminum oxide or the reversible monoclinic to tetragonal transition that occurs in zirconium dioxide, can result in major volume changes as well as significant undesirable changes in properties. Finally, since interdiffusion and high-temperature reactions can alter local chemistry, microstructure, and properties -- again usually in a detrimental manner --- the thermodynamic stability of the fiber and matrix combination is a key to long-life composites.

Figure 4 shows the density of a number of the compounds of interest as fibers as well as the densities of PMC (polymer matrix composites), some of the aluminides (FeAl, NiAl), superalloys and copper, and finally some of the extremely dense refractory metals.

Figure 5 illustrates the various issues that must be considered when discussing fiber strength. First, short-time tensile strength is, of course, degraded at high temperatures. More critical degradation stems from physical damage to the fibers during fabrication and any matrix reactions that result from the time-temperature exposure related to composite consolidation. Here local flaws, primarily surface in nature, control fiber strength. Secondly, the long-time, and thus life-controlling, issues are fiber creep (primarily plastic deformation) and the matrix reactions previously discussed. In this case, fiber microstructure controls strength.

Figure 6 presents some coefficients of thermal expansion (CTE's) of a number of the compounds of interest for fibers. Remember that because the expansion of a compound or metal is usually not linear, such CTE's are merely an approximation of total behavior. Thus, when thermal mismatch issues are considered, the actual values at any particular temperature must be examined. Finally, figure 7 outlines the methods used to assess the thermodynamic compatibility of a fiber and a matrix.

There are currently three major classes of high-temperature, high-performance fibers: carbon fibers, oxide fibers, and fibers of other materials including intermetallic/interstitial compounds and metals. Figure 8 schematically presents the strength-versus-temperature curves for these fiber types. Carbon fibers, as well as fibers of tungsten and molybdenum, react with oxygen in air to form gaseous and/or weak solid oxides. Such behavior severely limits their use temperature; in an inert atmosphere or vacuum both carbon and refractory metal fibers have use potential to well above 3000 °C. The common oxide fibers, of course, have much better resistance to oxidation because they are already fully oxidized. However, their strength at high temperature is generally only modest unless the fibers are single crystals of the oxide. Currently, the class of fibers with the most promise at high temperatures consists of those compounds that have reasonable -- but not outstanding -- high-temperature strength and yet have reasonable oxidation resistance as well. In general, most of these fibers consist of very small (and usually stable) grains although some involve ultrasmall grains or are nearly amorphous. Some fibers, those that are formed by a chemical vapor deposition process on a small-diameter core fiber, show grain structures that are columnar and perpendicular to the core. And, as previously indicated, some fibers are grown so as to be single crystals.

The preceding discussion shows that the fiber process also provides a way to classify fibers. Figure 9(a) presents a variety of schematic representations of fiber production via precursor approaches. In almost every case a precursor (ranging from selected petroleum pitches to specifically compounded polymers) is forced through a series of tiny orifices to produce some fibrous shape that is then heated, pyrolyzed, or cured to form the fiber. In some cases, additional steps such as heat treatments and stretching/heating are added to achieve the final product. In figure 9(b) a number of direct conversion processes are also schematically displayed. Here molten oxide or polymer materials are forced through small orifices to form fibers. Alternatively, metal rods are extruded and then the resulting wire is drawn down to fiber dimensions. Another approach involves starting with a core fiber as in chemical vapor deposition or with a seed crystal as in melt drawing, laser float zone growing, etc.

Fibers can also be differentiated based on their diameter. Such differences are shown in figure 10. Generally, large-diameter fibers are incorporated in ductile matrices. In this way the fiber volume fraction can be kept high to exploit the superior properties of the fibers, and yet the spacing between fibers can also be maximized to exploit the inherent ductility of the matrix. An additional factor is the need for strong fiber-to-matrix bonding so as to tranfer load on the matrix to the stronger fibers. In brittle matrices, however, small-diameter fibers are sought, since close fiber spacing is desired to bridge small process- and service-initiated cracks that could result in catastrophic failure of a loaded ceramic structure. The other issue facing composites consisting of brittle matrices is that the fiber-to-matrix bond should be rather weak, since it is desirable that the cracks deflect around the fibers during matrix fracture ("graceful failure").

Finally, as shown in figure 11, layups made of individual single fibers are differentiated from composites made from two-dimensional woven cloth as well as from layers of such cloth stitched together into three-dimensional products. Generally, fibers are also "sized" or coated with an organic or inorganic material to improve their processibility. Figure 12 presents some schematic versions of these coatings. In the case of high-temperature fibers, diffusion barriers may be considered to control thermodynamic activity differences. Fibers can also be coated to improve their wettability if the fabrication process involves a molten metal, a glass, or a ceramic infiltrant. More recently, coatings have been found to heal surface defects and thus raise the fracture strength of fibers by shifting the failure site from the surface to an internal site (where there are smaller flaws that require higher loads to propagate cracks). In addition, the concept of a relatively thick coating to provide strain accommodation (compliant layer coatings) has been pursued. Such coatings can also offer improved protection to the fiber during fabrication.

Figure 13 shows one approach for fiber selection. First, the fiber must have useful high-temperature properties. If it does, the issue of thermal expansion match can be examined. If a poor match exists, the possibility of using a compliant layer can be explored. For those compositions that pass through both screens, fiber-matrix compatibility must still be considered. If the potential for rapid interdiffusion exists, a diffusion barrier coating must be considered. Few fibers can pass through all three screens successfully.

Figure 14 indicates the amount of fiber that might be needed to make a component. Depending on the fiber diameter and the volume fraction of fiber used in a composite, for just 1 in.^{3}, fiber requirements range from 0.1 to 16 miles. Thus, fiber production processes must be capable of providing large quantities of continuous fiber. In addition, cost typically will be the ultimate factor in fiber selection and as can be seen, except for very costly single-crystal fibers, fibers can currently be produced at costs that are reasonable for aerospace applications.

Fibers Now Available in the United States and Japan

Table I lists the commercial and experimental silicon carbide-based fibers available from both the United States and Japan. Note that Nicalon (15 µm or micrometers in diam) and Tyranno fibers (9 to 11 µm in diam) from Japan are available from U.S. distributors (Dow Corning and Textron, respectively) who are both fiber manufacturers themselves. These fibers are both derived from polymer precursors. Textron's SCS family of fibers is produced by chemical vapor deposition onto a carbon core and are much larger in diameter (142 and 75 µm).
SCS fibers are available with a variety of surface coatings in order to tailor the interface to the selected matrix material. Dow Corning is exploring a small (10 µm) diameter SiC fiber from a polymer precursor under sponsorship of NASA Lewis Research Center. Likewise, NASA Lewis is sponsoring research at State University of New York (SUNY at Buffalo) to develop a 15-µm-diameter SiC fiber produced by chemical vapor deposition. Similar work is also being conducted at Rensselaer Polytechnic Institute (RPI). Figure 15 is an extraction of Nippon Carbon Company's literature and shows the polymer precursor and fiber production steps as well as some company information on the finished products. Table II lists some literature values for key Nicalon fiber properties. This material is available in a variety of yarns, woven cloth, rope, paper, mat, etc.

Table III lists the commercial and experimental silicon nitride-based fibers available from both the United States and Japan. Both the United States, because of the Dow Corning fibers identified as HPZ and MPDZ, and Japan, because of Tonen's silicon nitride and the new silicon boronitride fibers, have such fibers. Furthermore, since Mobil and Exxon each own 25 percent of Tonen, there is some U.S. commercial involvement in all silicon nitride-based fibers. Figure 16 is a compilation of information and pictures from Tonen's literature. It shows the fiber production process -- fiber spinning and final product (enlarged view). Although the Tonen fiber is viewed as developmental, figure 17 shows some property data, indicates the need to maintain low amounts of excess silicon to prevent crystallization of the normally amorphous fiber, and shows that the use temperature of this fiber is no more than 1100 °C. Figure 18 shows the process described by Tonen to produce its new silicon boronitride fiber which was stated to be amorphous to 1700 °C and to have an elastic modulus of about 200 GPa (only data provided).

Table IV lists the commercial and experimental oxide-based fibers available from both the United States and Japan. It is interesting to note the large number of oxide fibers produced in the United States. Even Altex by Sumitomo Chemical is available from Textron, its U.S. distributor. Most of the fibers listed are produced either from polymer precursors or by a sol-gel or slurry process. The Saphikon fiber (250 µm diameter) is, however, produced by melt extraction, and the NASA Lewis experimental fiber is made by a laser float zone (LFZ) process. The latter two fibers are between 100 and 250 µm in diameter, but most of the oxide fibers fall in the range 10 to 30 µm. Figure 19 is a further compilation of Sumitomo literature showing the polymer precursor process used to achieve this gamma alumina fiber and the very small grain sizes that are achieved. Figure 20 is a second compiliation of the Sumitomo literature showing some of the mechanical property data. The reason for the fiber's useful limit being about 1100 °C is the decomposition of the silica-rich gamma alumina to alpha alumina and mullite at that temperature. The Altex fiber is also available in a variety of forms including rovings and woven (plain and satin) materials.

Finally, as shown in Table V, a number of other fibers are being developed or are available commercially. In general, however, the few fibers of this nature that we came across in Japan were identified with universities, and thus may be further from commercial production.

A large number of carbon fibers are produced in the United States as well as in Japan. They can be differentiated by their starting material -- either a wide range of petroleum pitches or polyacrilonitrile (PAN). Among pitch-derived fibers are general-purpose (GP) pitch fibers, which are usually short and of lower strength. A second class of pitch fibers encompasses a variety of high-performance, high-strength fibers. These are further differentiated by HT (high tensile strength), HM (high modulus), and UHM (ultrahigh modulus). Japan produces over 5000 tons of carbon fiber per year but uses only about half that amount for its own products. Table VI makes an attempt to list some (but not all) of the experimental and commercial carbon fibers available in the United States and Japan. The Japanese have not only developed the PAN approach but have a strong capability in pitch-based fibers. For example, Granoc is Nippon Oil Co. Ltd.'s product involving a 10-µm-diameter pitch-based fiber. They reported production capacity up to 50 tons/year from their Yokohama Plant. Figure 21, data extracted from Nippon Oil Co. literature, shows some mechanical property data for Granoc. Figure 22 shows some of the forms in which the fiber is available and some of the applications for the fiber. Figures 23 and 24 show some similar information extracted from Tonen Corporation's literature on its Forca carbon fiber. The first figure shows some of the forms in which it is available and the second gives some typical properties.

A few high-temperature, high-strength refractory metal fibers are available in the United States as shown in table VII. The primary application for such fibers is in incandescent light bulbs. These fibers are ductile and strong at high temperatures but are rapidly attacked by air. Thus, they have primary potential in nonoxidizing environments -- as in space applications -- but if properly protected may be of use as ductile strengthening phases in other applications as well. We did not encounter any information that there was work under way on such fibers in Japan.

Fiber Summary

Figure 25 is a plot of room-temperature tensile strength versus modulus for a variety of the fibers previously presented. Note that even at room temperature, few of the current fibers have strengths near or above 3 GPa combined with moduli above 300 GPa. However, to achieve the full potential of advanced composites, fibers are needed with such properties not only at room temperature but at temperatures to 1600 °C. Figure 26 is a summary of the properties of a number of classes of known fibers as a function of temperature. Even the short-time tensile properties drop off in the 1000 to 1200 °C range. Thus, we can expect that long-time creep strengths will be substantially lower. This means considerable effort will be required by both countries to improve their fibers so as to reap the benefits of low-density, high-strength composites for high-temperature aerospace applications. As shown in figure 27, an effort has been started in Japan to develop the improved production technology to convert current (and surely) future fibers to commercial structural forms even though optimum fibers are yet to be developed.

Whiskers

Table VIII shows some of the small number of different whiskers produced by the United States and Japan. In general, it has recently been recognized that such whiskers require careful handling owing to potential health issues, and thus not much interest was expressed in expanded whisker research by the Japanese companies that we visited.

Final Remarks

Figure 28 presents this author's personal view of one possible scenario that might be followed by the Japanese in their efforts to expand their commercial advanced composites business. Currently, they have a national research effort under way on functionally graded materials (see a later section of this report). That effort could contribute to building skills in applying thin coatings on fibers by such methods as chemical vapor deposition and in analyzing very thin fiber/matrix interfaces. Such an effort significantly supports the ongoing programs in fiber development and composite application. This research can be coupled with an evolving industrial capability to manufacture composites for mass markets. In combination, such skills and abilities indicate that Japan will be positioned to be a strong competitor to the currently fragmented, small U.S. capability in manufacturing advanced high-temperature composites.

Figure 29 compares our recent findings with those of the 1988 survey (published in November 1989) by the Office of Naval Research (ONRFE 7, "Inorganic Composite Materials in Japan: Status and Trends" M.J. Koczak et al.). One key observation is that the recent efforts by the Japanese to establish joint programs on supersonic/hypersonic propulsion systems with U.S. engine companies, coupled with the knowledge gained in the completed Jesedai program on engine composites, would certainly strengthen Japan's abilities to eventually produce and export commercial aircraft engines. A second observation is that Japan has recently started a national effort to conduct research on high-temperature composites for extreme environments. Such composites will be the basis for the high-value-added components that must be developed to enable commercially viable future aircraft engines. They will be the "computer chips" of future aerospace propulsion and power hardware.

Better high-temperature fibers are the key to high-performance, lightweight composite materials. However, current U.S. and Japanese fibers still have inadequate high-temperature strength, creep resistance, oxidation resistance, modulus, stability, and thermal expansion match with some of the high-temperature matrices being considered for future aerospace applications. In response to this clear deficiency, both countries have research and development activities under way. Once successful fibers are identified, their production will need to be taken from laboratory scale to pilot plant scale. In such efforts it can be anticipated that the Japanese decisions will be based on longer term criteria than those applied in the United States. Since the initial markets will be small, short-term financial criteria may adversely minimize the number and strength of U.S. aerospace materials suppliers well into the 21st century. This situation can only be compounded by the Japanese interests in learning to make commercial products with existing materials so that when the required advanced fibers eventually do arrive, their manufacturing skills will be well developed.

TABLE I. - SiC FIBERS

(a) United States

Fiber	Company/University
Nicalon[a] (Si-C-O)	Dow Corning (U.S. distributor for Nippon Carbon)
Tyranno[a] (Si-Ti-C-O)	Textron (U.S. distributor for Tyranno)
SCS-2,6,9,10[c] (carbon core, 142-μm diam)	Textron
Experimental[a,b] (10-μm diam)	Dow Corning
Experimental[b,c] (15-μm diam, 7-μm carbon core/tow)	SUNY
Experimental[c]	RPI

(b) Japan

Fiber	Company/University
Nicalon[a] (Si-C-O) 14-μm diam): NL-200 (ceramic grade) NL-400 NL-600	Nippon Carbon
Tyranno[a] (Si-Ti-C-O, 9- to 11-μm diam)	UBE

[a] Derived from polymer precursor.

[b] Research and development effort supported by NASA Lewis.

[c] Produced by chemical vapor deposition.

TABLE II. - REPORTED PROPERTIES OF NICALON FIBERS

Density, ρ, g/cm3	2.6
Tensile strength, GPa	2.5-3
Modulus of elasticity, E, GPa	180-200
Coefficient of thermal expansion, CTE, 10^{-6}/°C	3.1
Maximum use temperature, °C	1200

TABLE III. - SILICON NITRIDE FIBERS

(a) United States

Fiber	Company
HPZ[a] (8- to 15-μm diam)	Dow Corning
MPDZ[a] (10- to 20-μm diam)	Dow Corning
SiN[a]	Tonen[b]
SiNB[a]	Tonen[b]

(b) Japan

Fiber	Company
SiN[a] (10-μm diam)	Tonen[b]
SiNB[a]	Tonen[b]

[a] Derived from polymer precursor.
[b] Ownership, 25 percent Mobil and 25 percent Exxon.

TABLE IV. - OXIDE FIBERS

(a) United States

Fiber	Company
Altex[a](Al_2O_3-15SiO_2)	Textron (U.S. distribution)
Saphikon (Al_2O_3 monocrystal, 250-µm diam)	Saphikon
Nextel (10- to 12-µm diam):	3M
312 (glass SiO_2-Al_2O_3-B_2O_3)	
440 (glass SiO_2-Al_2O_3-B_2O_3)	
480 (glass SiO_2-Al_2O_3-B_2O_3)	
Z-11 (ZrO_2/SiO_2/Al_2O_3)	
PRD-166(Al_2O_3-ZrO_2, 20-µm-diam, slurry)	Dupont
FP(Al_2O_3, 20-µm diam, slurry)	Dupont
Experimental (Al_2O_3, 100- to 200-µm diam, LFZ)	NASA Lewis
Experimental (Al_2O_3, 25- to 50-µm diam, polyxyl)	3M; Dupont
ZYT(ZrO_2, 3- to 6-µm diam)	Zircar

(b) Japan

Fiber	Company
Altex[a](Al_2O_3-15SiO_2,10- and 15-µm diam)	Sumito Chemical Company

[a] Derived from polymer precursor.

TABLE V. - SOME OTHER FIBERS

(a) United States

Fiber	Company/ University
Nb_2Be_{17}[a,b](125- to 250-µm diam)	Textron
CrB_2[a,b](125- to 250-µm diam)	P&W
Ti_xAlC [b](Mo core, 200-µm diam)	Textron
CrB_2[b](125- to 250-µm diam)	SUNY
HfN	Ultramet
TiC	Ultramet
B/BN	Ultramet
TiB_2[b](Mo core, 70-µm diam)	SUNY
TiB_2[b] (Mo core)	Amercom
TiB_2[b](Mo core, 65-µm diam)	RCI

(b) Japan

Fiber	Company/ University
$BaTiO_3$ (5- to 10-µm long)	Kyoto University
B or B_4C	Tokyo University (Dr. Okura)

[a] Research and development effort supported by NASA Lewis.

[b] Produced by chemical vapor deposition.

TABLE VI. - OVERVIEW OF SOME CARBON FIBERS

(a) United States

Fiber	Company
Magnamite[a](Multiple variations: HMS,HMU,AS1,AS2,AS4,AS6, IM6,HTS)	Hercules
HDG	Fiber Materials, Inc.
Microfil 40	Fiber Materials, Inc.
Microfil 55	Fiber Materials, Inc.
Celion-base structural materials[a](GY-80, 1000, 3000, 6000, 12 000)	May be Japanese manufactured
Torayca	Amoco (licensee)
Panex (30, 30Y/300D, 300Y/800D, 30R)	Stackpole
Fortafil[a](3(C),3(0)5(0), OPF(C),OPF(0))	Great Lakes Carbon
Thornel[a](T-40,T-50,75, T-300,400,T-500,700)	Amoco
PAN-50[a]	Amoco
VSA-11[b](VS-0032)	Amoco
P-VSB-32	Amoco
P-VS-0053[c]	Amoco
Grafil (IMS, HM-S/10K, HMS/6K, XA-S)	Hysol Grafil Co.
Hitex[a]	Hitco Materials, Inc.
Hispan[a]	Hercules (ownership, 50 percent Sumitomo)
Experimental[c]	Dupont
Experimental[c]	Amoco

[a] Polyarilonitrile based.
[b] Mesopitch based.
[c] Pitch based.
[d] Pitch precursor; Cherry process.

TABLE VI. - Concluded.

(b) Japan

Fiber	Company
Petroka[a](HM50,HM60,HM70)	Kashima Oil
Petroka[b](20-μm diam, core for CVD)	Kashima Oil
Granoc[c](XN-40,XN-50,XN-60, XN-70)	Nippon Oil
Torayca[a](T-400,T-400H, T-800,T-1000,M-30,M-40, M-40J,M-46,M-46J,M-50)	Toray Industries (U.S. licensee, Amoco)
Besfight[a](ST-2,ST-3,IM-400, IM-600,HTA,HM35,HM40,HM45)	Toho Rayon Ltd.
Pyrofil[a](T-1,T-3,MM-1,LM-2, LM-5,HM-2,SM-1)	Mitsubishi Rayon
Donacarbo[d](F,S) F-140 (short and long) F-500 F-600	Osaka Gas Co.
Experimental[c](short fibers)	Kureha Chemical
Forca[c](FT 700,FT 500, UMH Tonen, HM, HT; 10-μm diam.)	Tonen
Hispan[a]	Sumitomo
Experimental[c]	Ueda
Carbalonz[a]	Nippon Carbon

[a] Polyarilonitrile based.
[b] Mesopitch based.
[c] Pitch based.
[d] Pitch precursor; Cherry process.

TABLE VII. - REFRACTORY METAL FIBERS AVAILABLE IN UNITED STATES

Fiber	Company
W-218CS	GE Phillips Elmet GTE (PM)
W-1ThO$_2$	GE Phillips Elmet GTE (PM)
W-3Re-Ge	--------------
W-Re-HfC	--------------
Mo-Hf-C	GTE
Mo-Hf-C (380-μm diam)	Metadyne Inc.

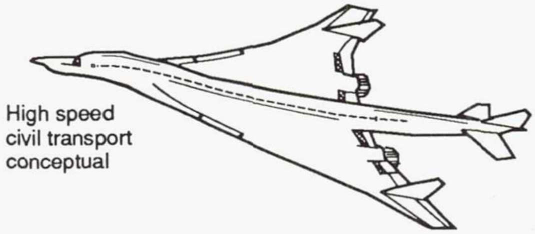
TABLE VIII. - WHISKERS

(a) United States

Fiber	Company
Tokawhisker (SiC_w)	Textron (U.S. distributor for Tokai Carbon)
SiC_w (0.3- to 0.6-μm diam, 3 to 24 μm long)	Advanced Composite Materials Corp.
Silar (SiC, 1-μm diam)	Arco Metals - Silag
VLS (SiC, 4- to 7-μm diam)	Los Alamos National Laboratory

(b) Japan

Tokawhisker (SiC_w, 0.1- to 1-μm diam, 10 to 100 μm long)	Tokai Carbon
$K_2Ti_6O_{13w}$(0.2- to 0.3-μm diam, 10 to 20 μm long, $\rho = 3.3$ g/cm^3, TS = 6.9 GPa, E = 274 GPa)	Otsuka Chemical
α- or β-Si_3N_{4w}(0.1- to 1.5-μm diam, 3 to 42 μm long)	Ube
SiC_w(1.5-μm diam, 1 to 100 μm long)	Toteho
Magnesca ((MgO)W, 2- to 10-μm diam, 100 to 1000 μm long)	Mitsubishi Mining and Cement
Alborex(($9Al_2O \cdot 2B_2O_3 \cdot Al_2O_3$)W, 0.5- to 1-μm diam, 10 to 30 μm long)	Shikoko Chemicals
($MgSO_4 \cdot 5MgO \cdot 8H_2O$)W(1-μm diam, 50 μm long)	Ube



	Conventional materials	*High* performance composites
Aprox. take-off Gross weight = lbs.	900,000	550,000
Aprox. Fuel for 5,000 mile flight* gals.	44,000	27,500

*Reduced fuel consumption and substantially lower NO_x, CO_2, etc. contingent on ceramic composite combustor and other advanced composite components.

Figure 1. – The difference.

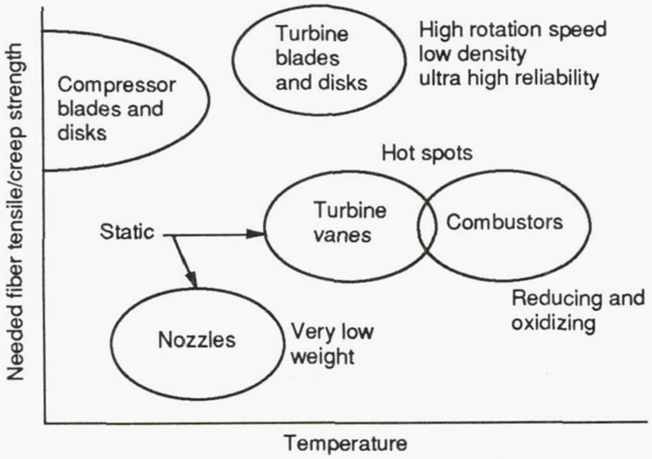


Figure 2. – Application requirements ⟶ Fiber and matrix requirements.

- Light weight

  $1/2\left(\frac{\text{Nickel alloy}}{\text{8 GMS/CC}}\right) + 1/2\left(\frac{\text{Aluminum oxide fiber}}{\text{\textasciitilde 4 GMS/CC}}\right) = \text{Composite \textasciitilde 6 GMS/CC}$

- High strength and stiffness-- RT ⟶ Maximum use temperature
- Good expansion match with matrix
- Phase and microstructure stability
- Very slow reaction with matrix

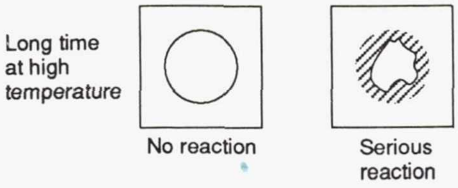


Figure 3. – Fiber goals.

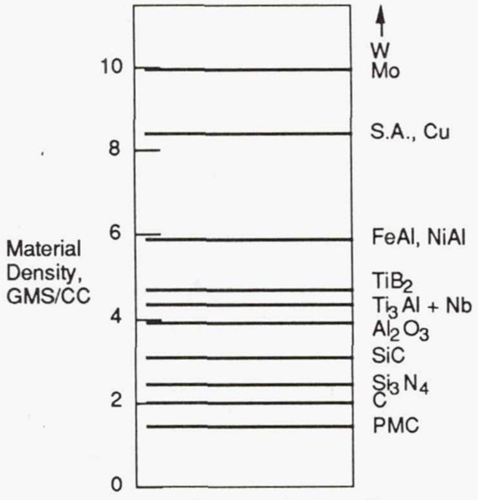


Figure 4. – Comparative Densities

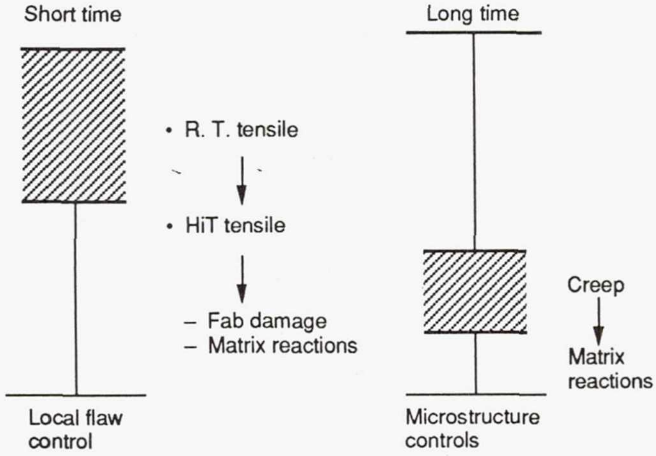


Figure 5. – Fiber strength.

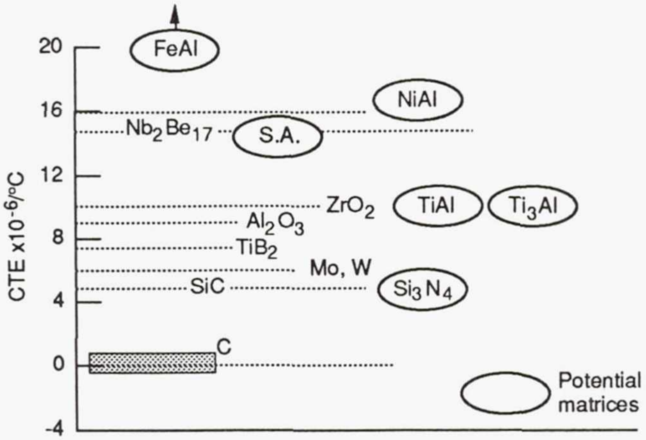


Figure 6. – Comparative coefficients of thermal expansion.

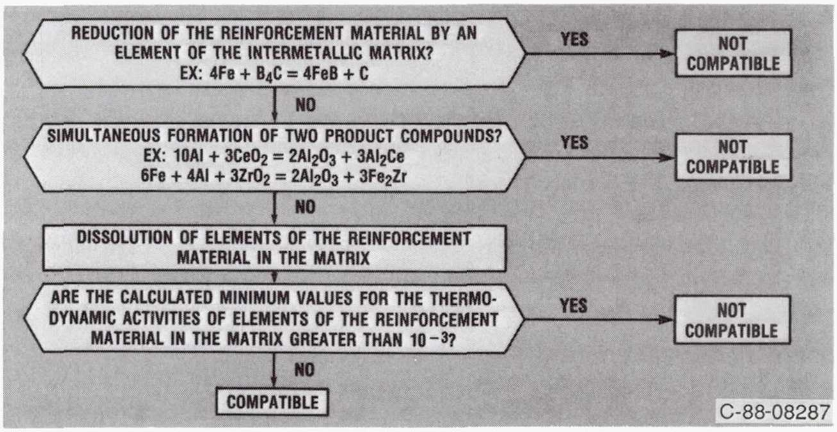


Figure 7. – Methodology of calculations to determine the compatibility of a reinforcement material in a given matrix.

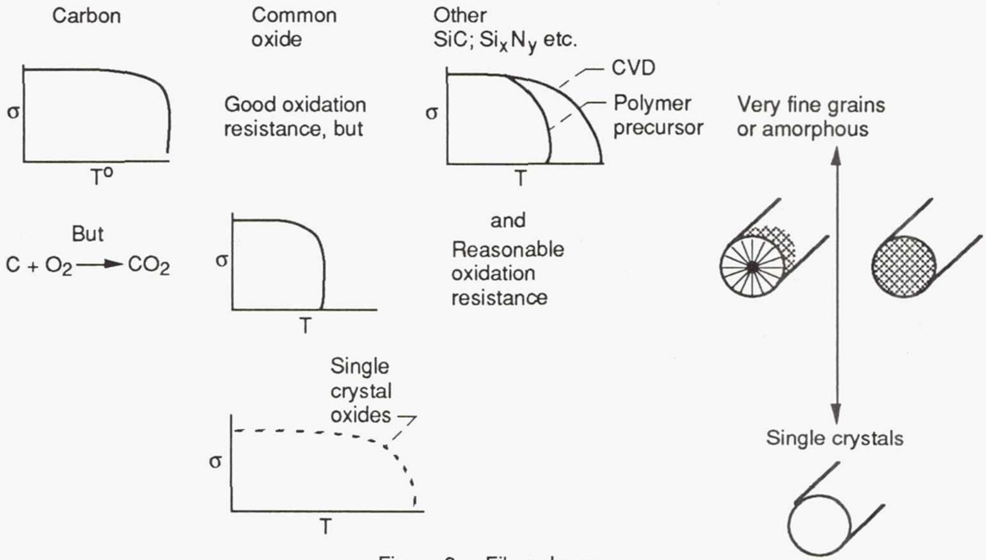
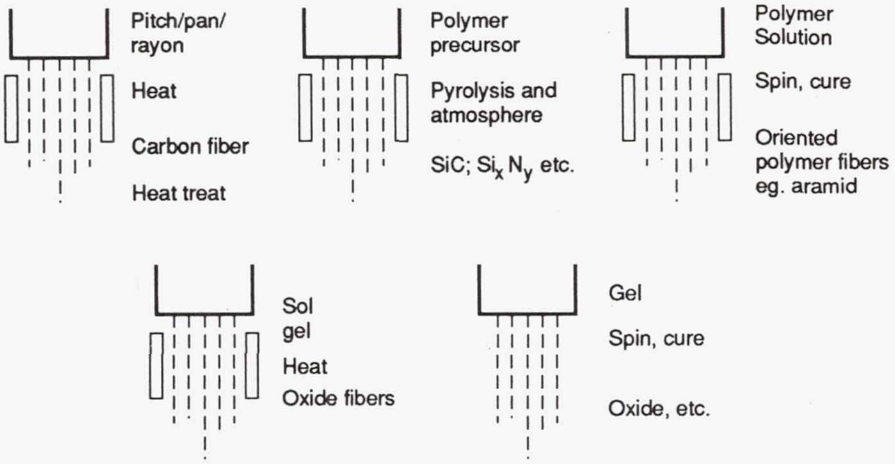
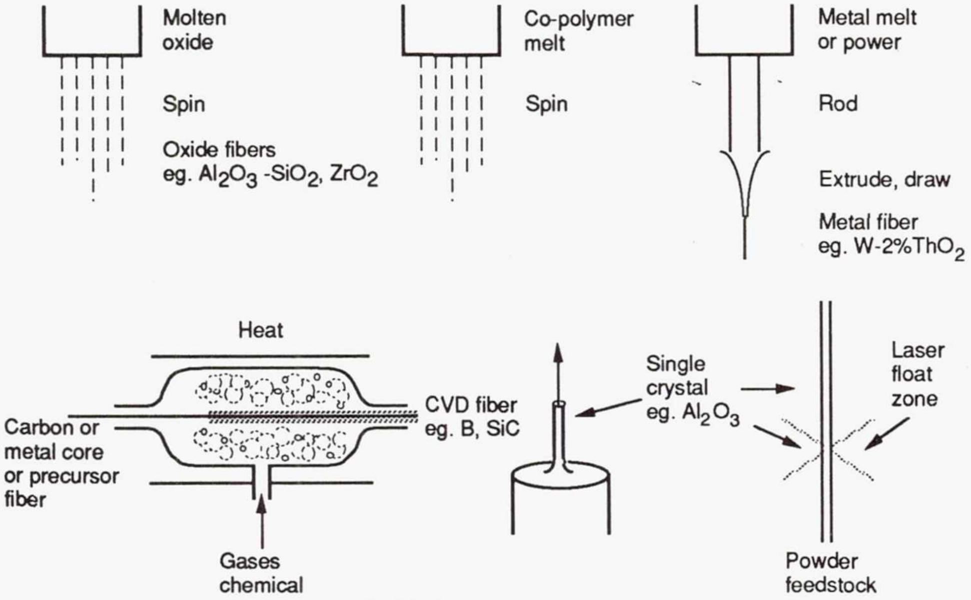


Figure 8. – Fiber classes.

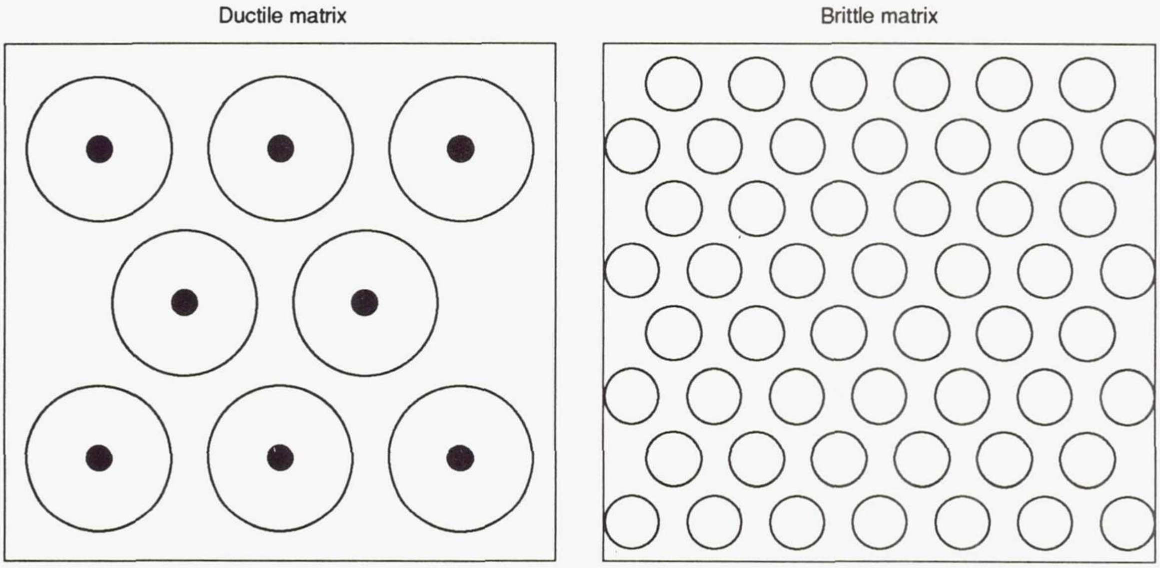


(a) Via precursor



(b) Via direct conversion

Figure 9. – Fiber processing concepts.

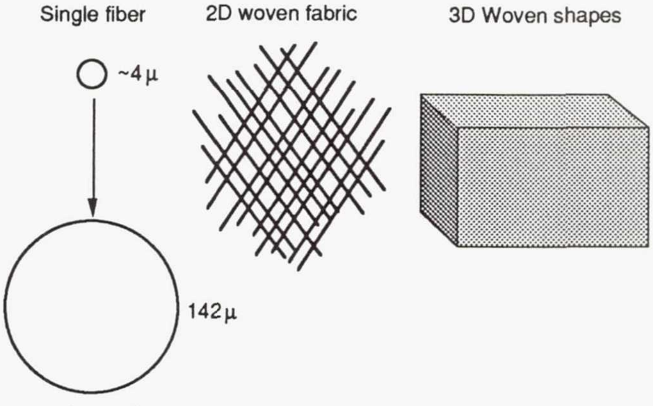


- Large fibers -- maximum interfiber space -- composite ductility
- Carry most of load
- Strong fiber/matrix bond
- 20-40μ* core carries no load

- Small fibers -- minimum interfiber space -- stop/slow cracks
- Carry load proportionately
- Poor bond -- permits fiber pull out and "graceful" failure

*μ = micrometer

Figure 10. – Different fibers for different matrices.



μ = micrometers

Figure 11. – From fibers to woven shapes.

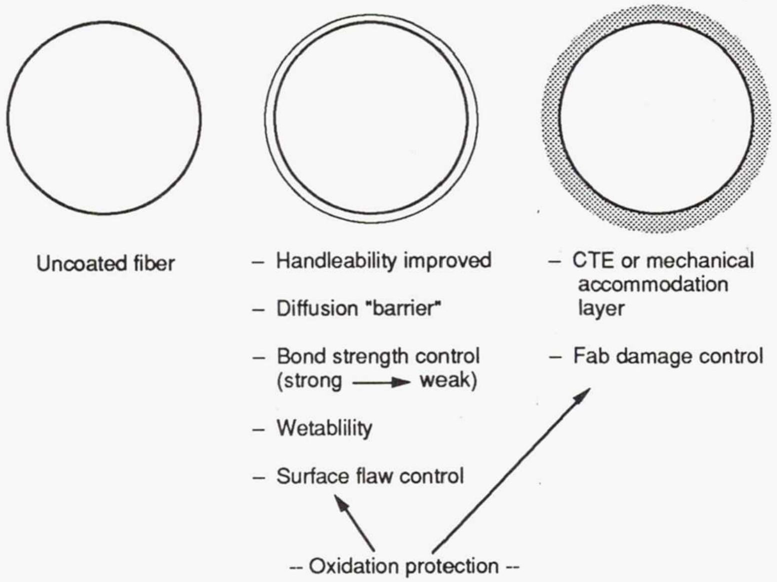


Figure 12. – Some types of fiber coatings.

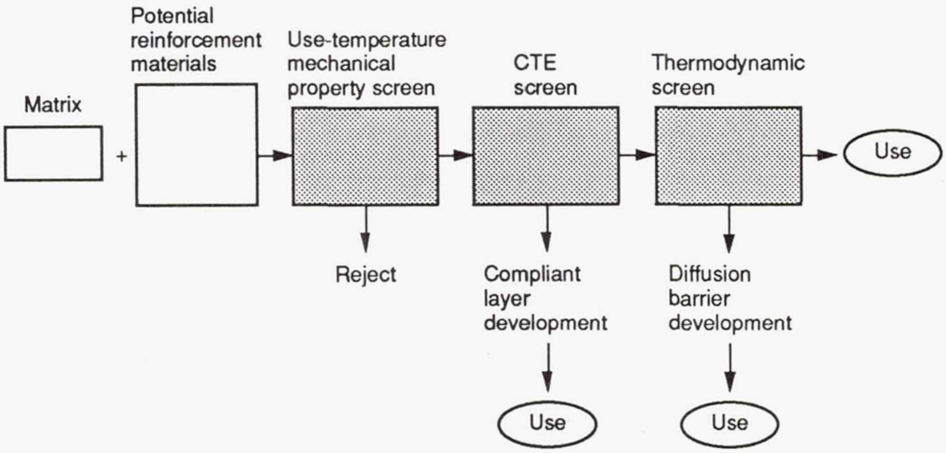


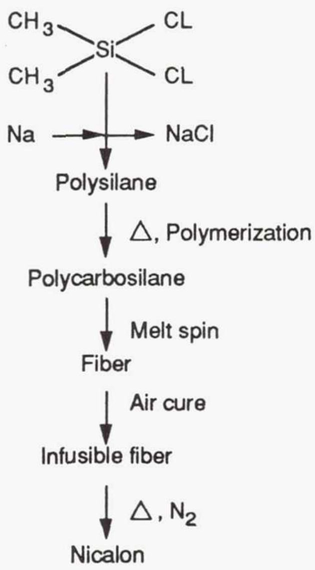
Figure 13. – Composite screening for eventual use.

For a composite of 50 V/O fiber	Approx. fiber length needed for 1 in.^{3} composite	Approx. cost * of fiber in 1 in.^{3} composite
• Al_2O_3 monocrystal (250 μ** dia.)	.1 miles	$7,500
• SiC CVD (142 μ** dia.)	0.3 miles	$ 132
• Al_2O_3 PP (250 μ** dia.)	~16 miles	$ 30
• SiC PP (250 μ** dia.)	~16 miles	$ 26

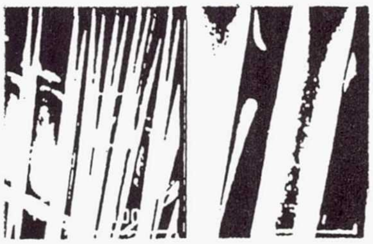
*Cost values after Hillig

**μ = micrometers

Figure 14. – A rough estimate of fiber use -- how much do we need and what can we afford?



Finished products of Nicalon®.



- Continuous fiber (multi-filament)
- Chopped
- Various woven products (cloth, braid, tape, rope)
- Various composite materials (MMC, PMC, CMC)

Products code number of Nicalon® continuous fiber.

Nicalon® (Silicon Corbide Continuous Fiber) is available in the following types designed for various applications.

type
NL - 200 series
NL - 300 series
NL - 400 series

Depending on the application of Nicalon® a suitable sizing agent can be chosen.

Product code number	Type of sizing agent
NL - XX0	NONE
NL - XX1	Use in PMC(epoxy)
NL - XX2	Use in MMC, CMC
NL - XX3	Use in PMC(BLMI)

12 and 15μ* fibers (continuous)
500 filament tows
~24,000 lbs./yr.
(24x10^6 miles/yr.)

*μ = micrometers

Figure 15. – Nicalon SiC fiber (extracts from Nippon Carbon Co. brochures).

Perhydropolysilazane
↓ + dissolve in organic solvent
Spinning dope
↓
Spin dry (perhydropolysilazane) fiber aligiomer
↓ H. T. in NH_3
Precursor
↓ H. T. in N_2
10μ* high purity silicon nitride fiber

Pilot plant level (after 9 years)
No production data

*μ = micrometers

Long continuous silicon nitride fiber.

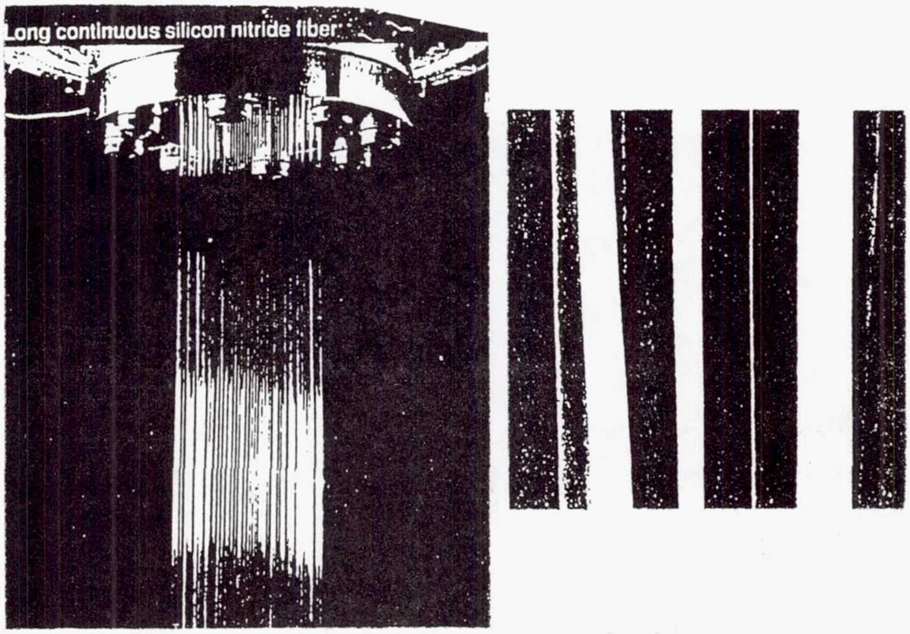


Figure 16. – Tonen Silicon Nitride Fiber (extracts from Tonen Corp. brochure).

Typical properties of silicon nitride fiber

Tensile strength	360 ksi (2.5 GPa)
Tensile modulus	36 msi (250 GPa)
Density	2.5 g/cc
Filament diameter	10 μm*
Coef. of thermal Exp.	1.5×10^{-6}/°C(up to 800 °C)
Crystal structure	Amorphous
Cont. use temperature	1200 (°C)
Composition (%)	Si, N, O, H, Si/N = 0.75-1.25 0<1.0%

Typical properties of perhydropolysilazane

Number average molecular weight	600-4000
Ceramic Yield (to 1500 °C)	85-93 wt%
Form	Liquid-solid
Solubility	Organic solvent
Composition	Si, N, O, H, Si/N = 0.75-1.25 0<1.0%

If excess Si/Si_3N_4:

0.47: α SiN to 1400 °C some βSi_3N_4 at 1500 °C

0.01: amorphous to 1400 °C small Si, α, β at 1500 °C

*μ = micrometers

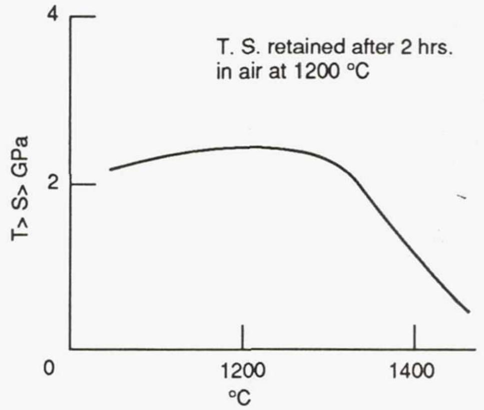
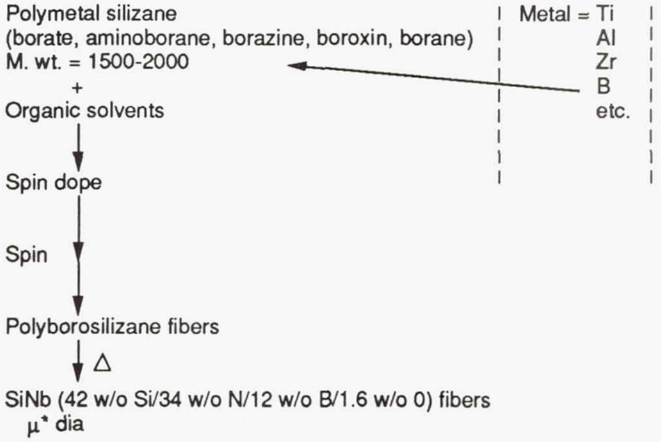
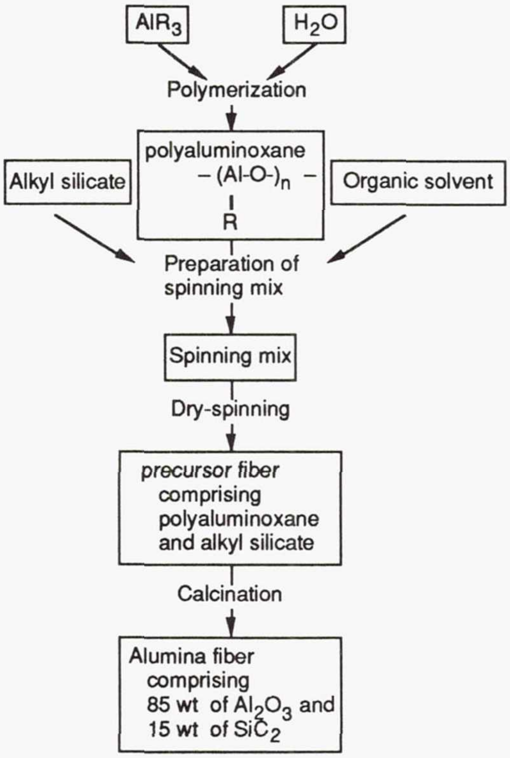


Figure 17. – Tonen SiN (extracts from Tonen brochures).



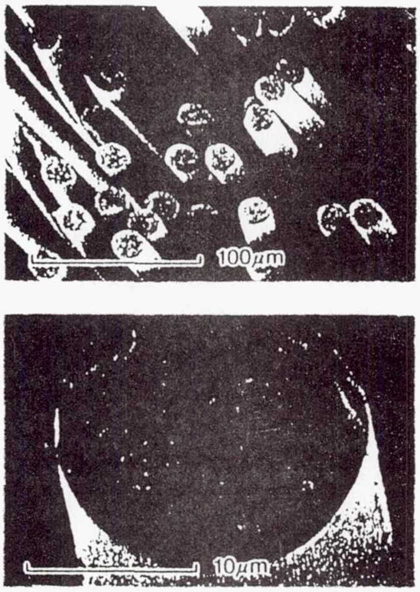
*μ = micrometers

Figure 18. – New Tonen SiNB fiber, Tonen Corp., U. S. patent 4,886,860 (12/12/89).

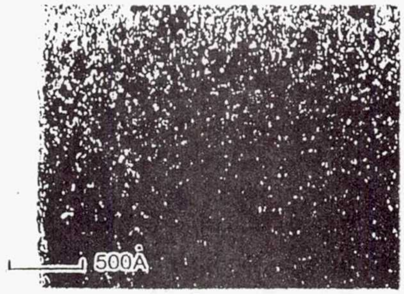


10 and 15µ* fibers (continuous)
500 and 1000 Filament tows (10µ-1000 only)
20,00 lbs/yr (14x10^6 miles)

*µ = micrometers

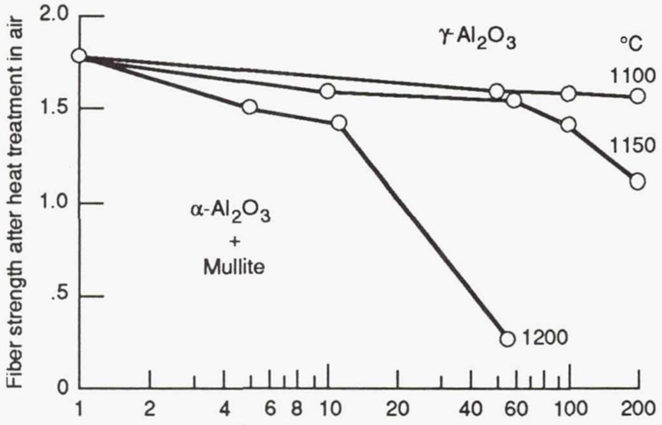


Scanning electron micrograph of "Altex".



Transmission electronmicrographof "Altex".

Figure 19. – "Altex" alumina fiber (extracts from Sumitomo Chemical brochures, U. S. patent 4,101,615 7/18/78.



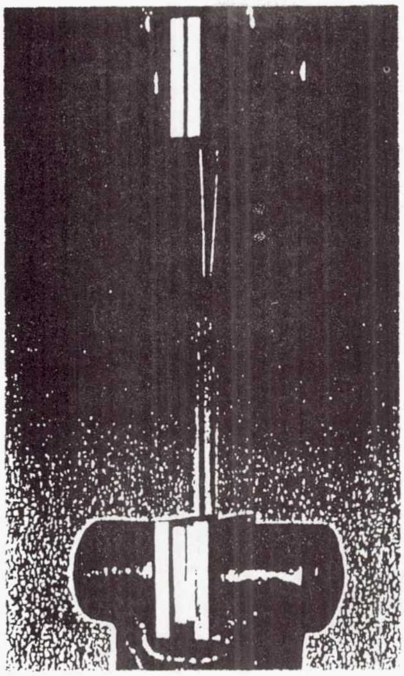
Fiber strength after heat treatment in air.

Properties of "Altex"

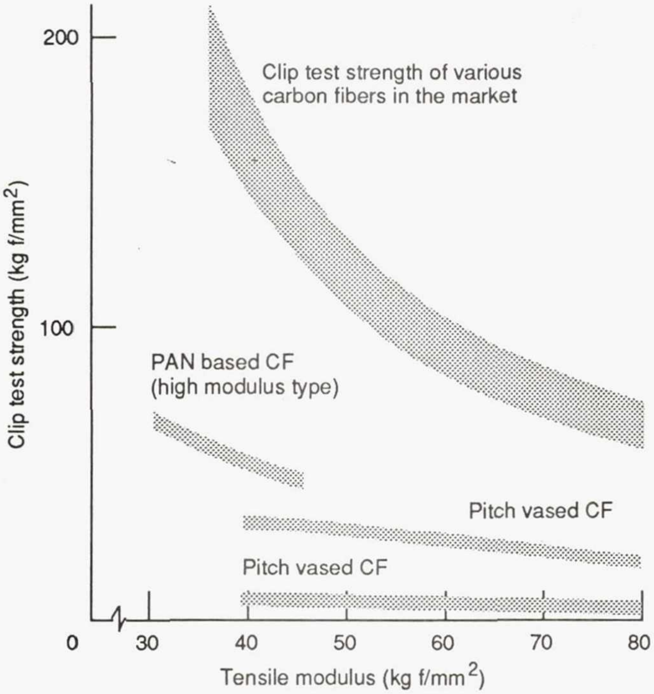
Chemical composition Al$_2$O$_3$ SiO$_2$ Impurity	 (wt.) (wt.) (wt.)	 85 15 <0.05
Crystal phase		γ-Alumina
Density	(g/cm)	3.3
Diameter	(μm)	10, 15
Filaments/yarn		500, 1000
Tensile strength	(GPa)	1.8
Tensile modulus	(GPa)	210
Maximum use temperature	(°C)	1,100*
Appearance	Colorless and transparent	
Refractivity index (No^{20})		1.67

* Temperature below which strength retention is higher than 90% for long period of time.

Figure 20. – "Altex' aluminia fiber properties (extracts from Sumitomo Chemical brochures).



GRANOC fiber Nippon oil.



GRANOC mechanical propertied	Special grades available for Aerospace use		
	XN-40	XN-50	XN-70
Modulus (10^{3}kg f/mm^2)	40	50	70
Strength (kg f/mm^2)	330	330	340
Elongation at failure (%)	0.83	0.66	0.49

Figure 21. – GRANOC carbon fibor (extracts from Nippon Oil brochures).

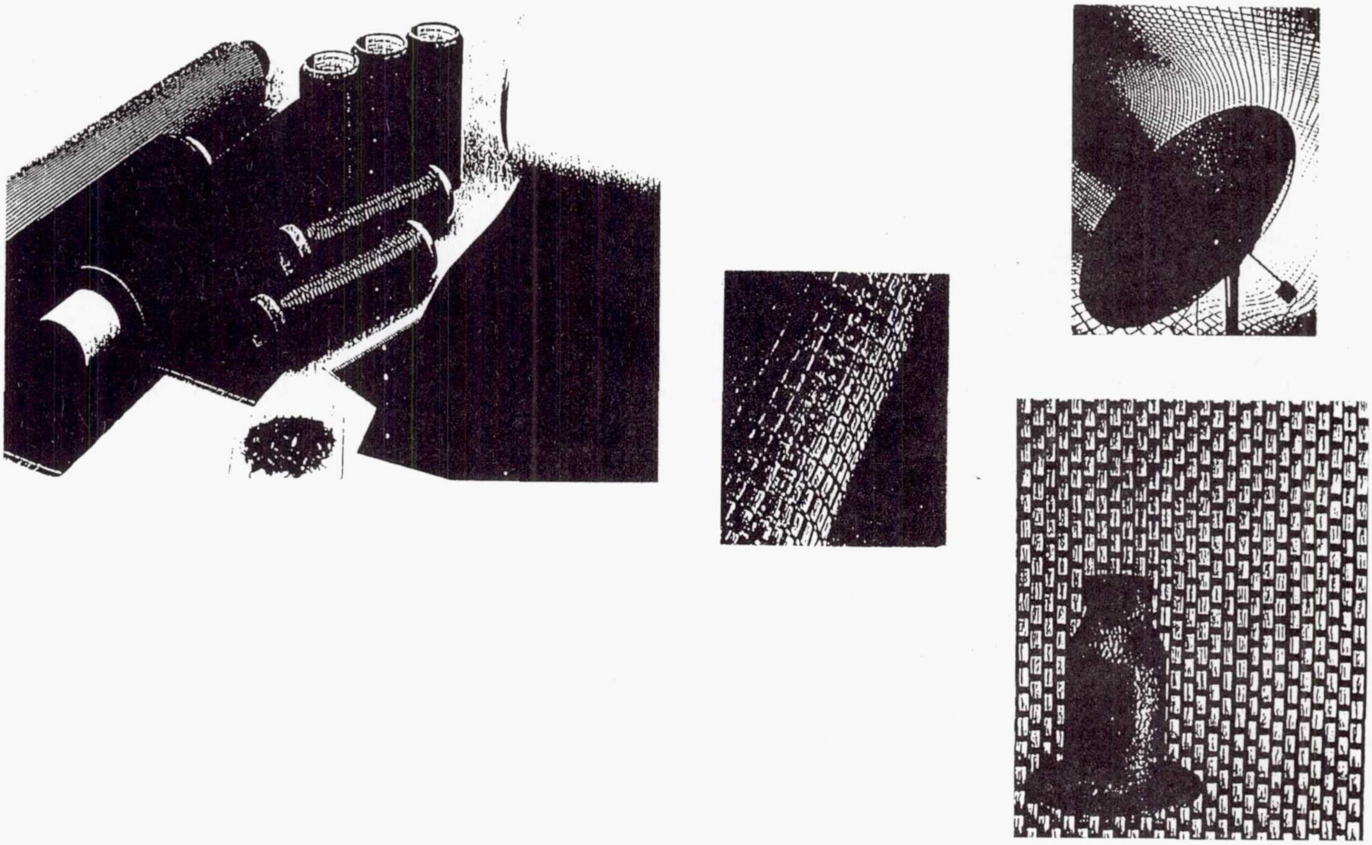
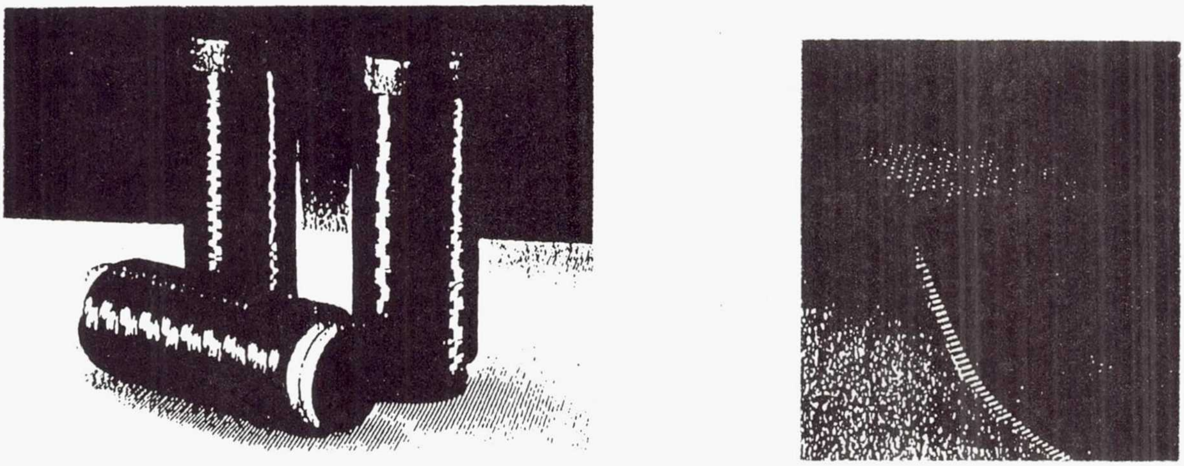
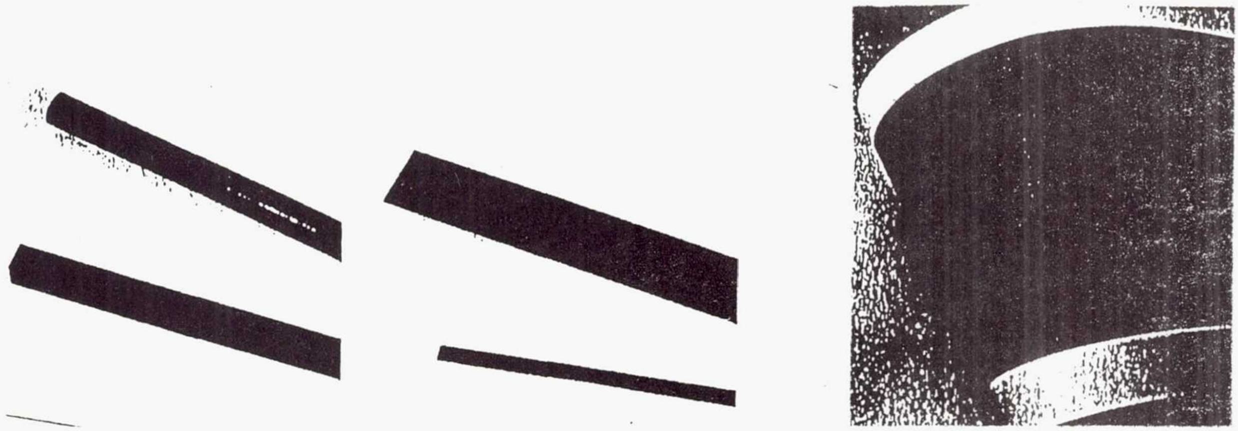


Figure 22. – GRANOC - Nippon oil (extracts from Nippon Oil brochures).



From pure, low viscosity pretroleum pitch.

Cloth



Pultruded pipe

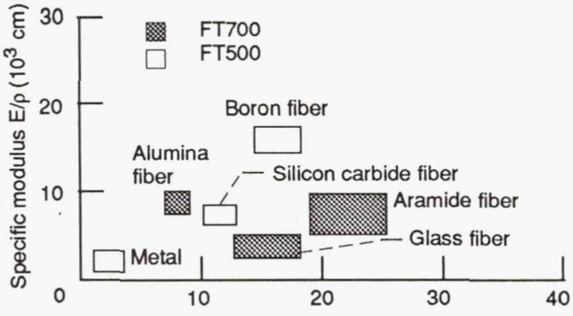
Pultruded pipe

Prepreg

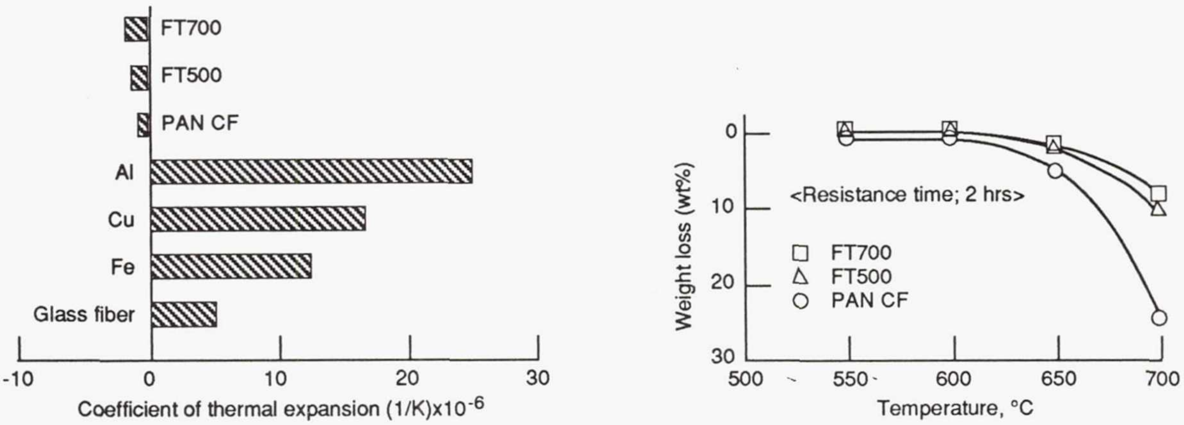
Figure 23. – FORCA carbon fiber (extracts from Tonen Corp. brochures).

	Properties	Units	FT700	FT500
Form of fiber	Filament diameter yield (3K base)	μ g/m	10 0.52	10 0.51
Physical properties	Density	g/cm	2.16	2.14
Mechanical properties	Tensile strength tendsile modulus elongation	MPa(Ksi) GPa(Msi) %	3300(470) 700(100) 0.5	3300(430) 500(70) 0.6

FORCA typical properities, Tonen Corp.



Specific strength, specific modulus.



Coefficient of thermal expansion

Oxidation resistance.

Figure 24. – FORCA typical properties (extracts from Tonen Corp. brochures).

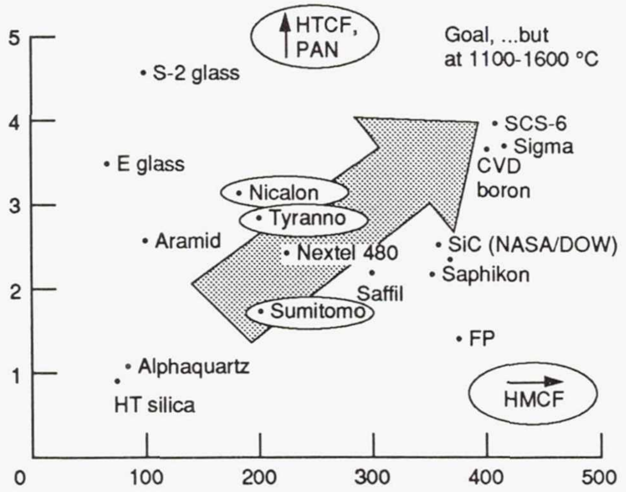


Figure 25. – Room temperature fiber properties.

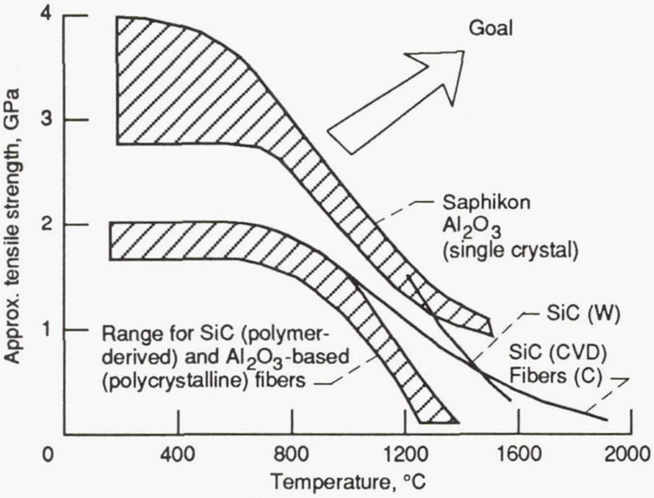


Figure 26. – High temperature fiber properties.

Capital: 70M¥ at start: to increase to 2B¥

70% – Japan Key Technology Center
9% – Mitsubishi Electric Corp.
9% – Nippon Steel Corp.
6% – Toyoda Automatic Loom Works, LTD.
3% – Arisana MFG. Co., LTD.
3% – Mitsubishi Rayon Co., LTD.

R&D of 3D weaving of strong inorganic, organic, and metallic fibers and of technology for structural use.

Figure 27. – A new corporation for composite fabrication: 3-D Composite Research Corporation, 1988.

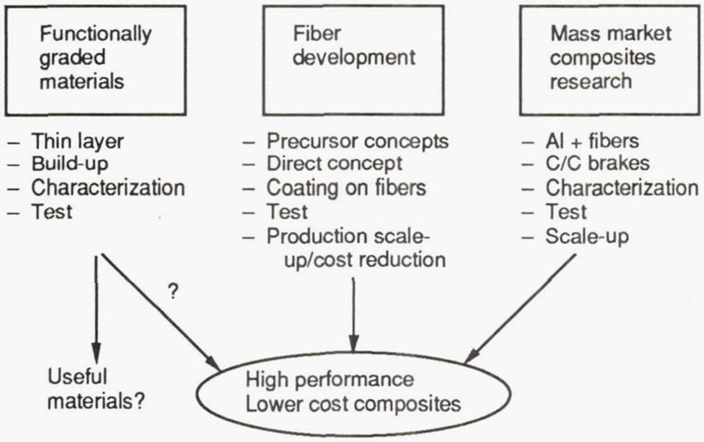


Figure 28. – A possible scenario.

- Japan invited U. S. engine companies to participate in (and get ¥ for) work on M3-5 transport.
- JESEDAI Program (1981-1988) completed and 1000 page handbook published.
- Tonen SiNB fiber announced and SiN being pilot-produced.
- FGM approach to fibers being pursued via CVD, etc., but still no major CVD fiber effort.
- Project for high temperature composites for use in severe environments started in 1989 (1989-1996) at ¥1B in '90.
- Decrease in whisker efforts due to health issues.

Figure 29. – Δ's from ONR assessment of 9/88 (published 11/89).

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16. Abstract

Better high temperature fibers are the key to high performance, light weight composite materials. However, current US and Japanese fibers still have inadequate high temperature strength, creep resistance, oxidation resistance, modulus, stability, and thermal expansion match with some of the high temperature matrices being considered for future aerospace applications. In response to this clear deficiency, both countries have research and development activities underway. Once successful fibers are identified, their production will need to be taken from laboratory scale to pilot plant scale. In such efforts it can be anticipated that the Japanese decisions will be based on longer term criteria than those applied in the US. Since the initial markets will be small, short term financial criteria may adversely minimize the number and strength of US aerospace materials suppliers to well into the 21st century. This situation can only be compounded by the Japanese interests in learning to make commercial products with existing materials so that when the required advanced fibers eventually do arrive, their manufacturing skills will be well developed.

17. Key Words (Suggested by Author(s)) Fibers Composites Material Strategy	18. Distribution Statement Unclassified – Unlimited Subject Category 24

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