Alumina Fibre FP [and Discussion]

A. K. Dhingra, N. Peacock, A. R. Ubbelohde and C. Manfre

Phil. Trans. R. Soc. Lond. A 1980 **294**, 411-417
doi: 10.1098/rsta.1980.0049

Phil. Trans. R. Soc. Lond. A **294**, 411–417 (1980)
Printed in Great Britain

Alumina fibre FP

By A. K. Dhingra

Pioneering Research Laboratory, Textile Fibers Department,
E.I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware 19898, *U.S.A.*

[Plate 1]

A new experimental inorganic fibre currently under development at the Du Pont Company is a continuous filament, polycrystalline α-alumina yarn designated Fibre FP. This fibre is suitable for reinforcing a variety of materials, especially non-ferrous metal castings because of a combination of properties such as high strength and modulus, stability at elevated temperatures, composite castability and potentially low cost.

Fibre FP, essentially > 99 % α-Al_2O_3, is made by a novel continuous ceramic fibre process utilizing low cost textile fibre spinning technology and is produced as a yarn containing 210 filaments.

The modulus of Fibre FP is 379 GPa (55×10^6 lbf in^{-2}) with a tensile strength of 1380 MPa (200000 lbf in^{-2}). The room temperature strength and modulus of the fibre are retained to about 1000 °C. Recently, higher strength FP fibres with a tensile strength of 2070 MPa (300000 lbf in^{-2}) have been demonstrated on a laboratory scale.

INTRODUCTION

Advanced fibre reinforced plastic composite materials based on high modulus fibres like graphite, Kevlar aramid are gaining wide acceptance because of their superior properties and potentially low cost of the reinforcing fibres. Fibre reinforced metals will be the next generation of advanced composite materials offering many advantages over fibre reinforced plastics including higher temperature capability, superior environmental stability, better transverse, shear, creep and impact properties. One of the major problems limiting the development of metal matrix composites has been the lack of a suitable low cost fibre for reinforcing metals. Du Pont is developing a new continuous ceramic fibre, based on aluminium oxide, called Fibre FP. This fibre is suitable for reinforcing a variety of materials, especially non-ferrous metal castings because of a combination of properties such as high strength and modulus at elevated temperatures, compatibility with molten metals, chemical inertness, composite castability and potentially low cost.

KEY FEATURES OF FIBRE FP

Fibre FP is a continuous filament polycrystalline α-alumina yarn with a density of 98 % of theoretical. The key features of Fibre FP shown in table 1 are its high modulus and strength which are retained to high temperatures. Another important feature of Fibre FP is outstanding compressive strength which translates into excellent compressive properties in composites. Since Fibre FP is a polycrystalline inorganic fibre, it has excellent transverse and shear properties compared to fibres like graphite or Kevlar aramid with oriented structures.

Fibre FP is essentially > 99 % purity α-Al_2O_3. Therefore, it has excellent chemical resistance and greater stability in molten metals than alumina fibres containing silica. Since it is an electrical non-conductor, it has very good corrosion resistance and does not induce galvanic corrosion in reinforced metals. We project its cost to be comparable or lower than high modulus graphite. The main drawbacks of Fibre FP are its relative higher density and brittleness in handling.

Table 1. Fibre FP: continuous filament polycrystalline α-Al_2O_3 yarn

Key features

high modulus and strength at elevated temperatures
high compressive strength
stable in molten metals
electrical non-conductor
cost comparable with that of graphite

Broad versatility in material reinforcement

(1) metals; Al, Mg, Pb; selective reinforcement of castings
(2) glasses and ceramics
(3) plastics: epoxy, polyimide (NR-150, PMR-15), hybrids with Kevlar

Fibre FP has a broad versatility in reinforcing a variety of materials including metals, plastics and ceramics. In the reinforcement of metals we have concentrated primarily on non-ferrous castings of aluminium, magnesium and lead. The fabrication and properties of Fibre FP reinforced castings are described in a companion paper 'Metal Matrix Composites Reinforced with Fibre FP (α-Al_2O_3)'. We believe the most effective use of Fibre FP is in selectively reinforcing portions of castings for improved stiffness, strength, wear resistance or high temperature capability. Fibre FP is also being evaluated for reinforcing glasses, ceramics and plastics such as epoxies or polyimides. Another attractive possibility is to improve the compressive strength and stiffness for hybrid resin composites containing Kevlar.

FIBRE FP PROCESS

Fibre FP is made by a novel continuous ceramic fibre process utilizing low cost textile fibre spinning technology. The schematic of the process is shown in figure 1. The Fibre FP process consists basically of three steps: slurry and spin mix preparation, yarn spinning and firing. First an aqueous slurry mix based on alumina and spinning additives is prepared. The viscosity of the solution is then carefully controlled by removing water to prepare a suitable spin mix from which the fibres are dry spun. The spun filaments are then fired in two steps, low firing to control shrinkage and flame firing to obtain a suitable dense α-Al_2O_3 fibre. The fired fibre is finally coated with a thin layer of silica to increase fibre strength (by healing surface flaws) and improve wettability with molten metals required for composite fabrication. A typical 500 g bobbin of Fibre FP produced in our experimental unit is also shown in figure 1.

FIBRE PROPERTIES

The silica coated FP fibres have relatively smoother surface, about 50 % higher tensile strength and improved wettability with molten metals than uncoated FP fibres. However, it appears that the silica coating on the fibres is dissolved by molten metal in composite

Fibre FP process

- Based on textile fibres spinning technology
- Potentially low cost

alumina H_2O spinning additives
\ | /
slurry mix
↓ dewatering (viscosity control)
spin mix
↓ dry spin
spun yarn
↓ low fire (shrinkage control)
fired yarn
| (1) flame firing (conversion to dense α-Al_2O_3)
↓ (2) silica coating (improve molten metal compatibility)
Fibre FP

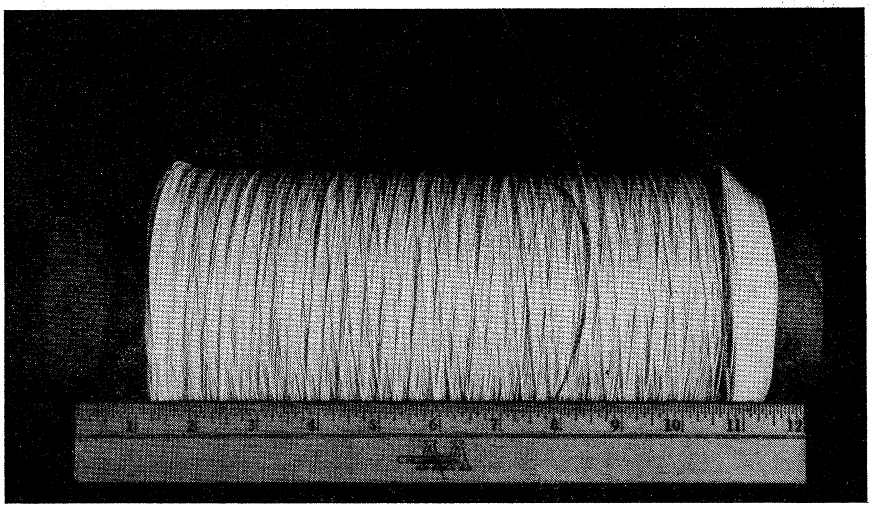

Figure 1. Fibre FP process, based on textile fibres spinning technology. This is a potentially low cost process.

fabrication and the effective strength of the fibre is reduced to that of uncoated FP fibres. The physical properties of Fibre FP are shown in figure 2. The average tensile strength of filaments tested at a gauge length of 6.3 mm ($\frac{1}{4}$ in) is 1380 MPa (200000 lbf in^{-2}). This is the fibre used for metals reinforcement and product development. The silica coated FP fibres having a tensile strength of about 1897 MPa (275000 lbf in^{-2}) are useful for resin reinforcement. We have also demonstrated a higher strength uncoated fibre with a tensile strength of 2070 MPa (300000 lbf in^{-2}) on a small scale in our laboratory. Theoretical models relating fibre strength to microstructure predict that strength greater than 3450 MPa (500000 lbf in^{-2}) should be achievable without change in modulus.

The compressive strength of Fibre FP (calculated from the composite compressive properties) is estimated to be about 6.9 GPa (1×10^6 lbf in^{-2}). The fibres have the same tensile and compressive modulus of 379 GPa (55×10^6 lbf in^{-2}). Density of the fibre is 3.9 g cm^{-2}, very close to the theoretical density of aluminum oxide. Diameter of the fibre is 20 μm, which is typical of a textile fibre. The fibre cross section is round and there are 210 filaments in the yarn bundle. Melting point of the fibre is unusually high. It is greater than 2000 °C. Therefore, the fibre has potential to reinforce high temperature materials. The filaments in the yarn bundle show a scatter in the tensile strength as shown by the frequency distribution in figure 1.

Fibre FP filament properties

tensile strength	1380 MPa (200000 lbf in^{-2})† 1897 MPa (275000 lbf in^{-2})‡ 2070 MPa (300000 lbf in^{-2})§
compressive strength	6.9 GPa (1×10^6 lbf in^{-2})‖
tensile and compressive modulus	379 GPa (55×10^6 lbf in^{-2})
elongation to break	0.4 %
density	3.95 g/cm^2 (0.143 lb in^{-3})
filament diameter	20 ± 5 μm
cross section	round
filaments in bundle	210
melting point	2045 °C (3713 °F)

† Used for metals reinforcement and product development.

‡ Silica coated fibre FP for resin reinforcement.

§ Uncoated fibre strength demonstrated on a laboratory scale. Theoretical models relating fibre strength to microstructure predict that strength greater than 3450 MPa (500000 lbf in^{-2}) should be achievable without change in modulus.

‖ Calculated from composite compressive properties.

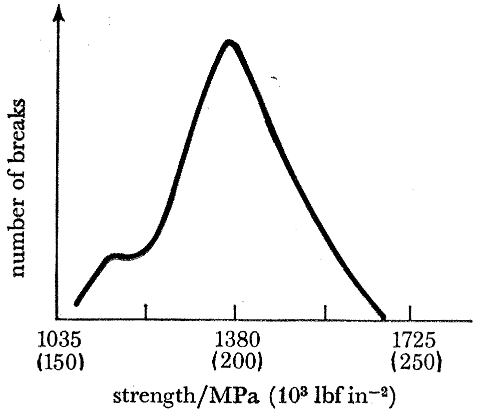

Figure 2. Fibre FP filament properties.

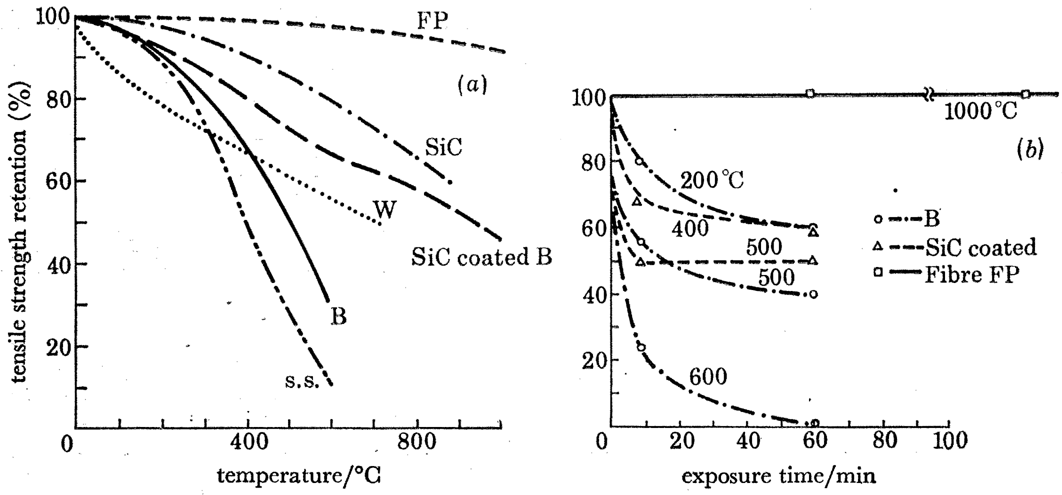

Figure 3. (a) Comparison of strength retention of Fibre FP at elevated temperature (s.s. = stainless steel). (b) Effect of exposure time in air on fibre strength at elevated temperatures. Fibre FP was unchanged after 300 h.

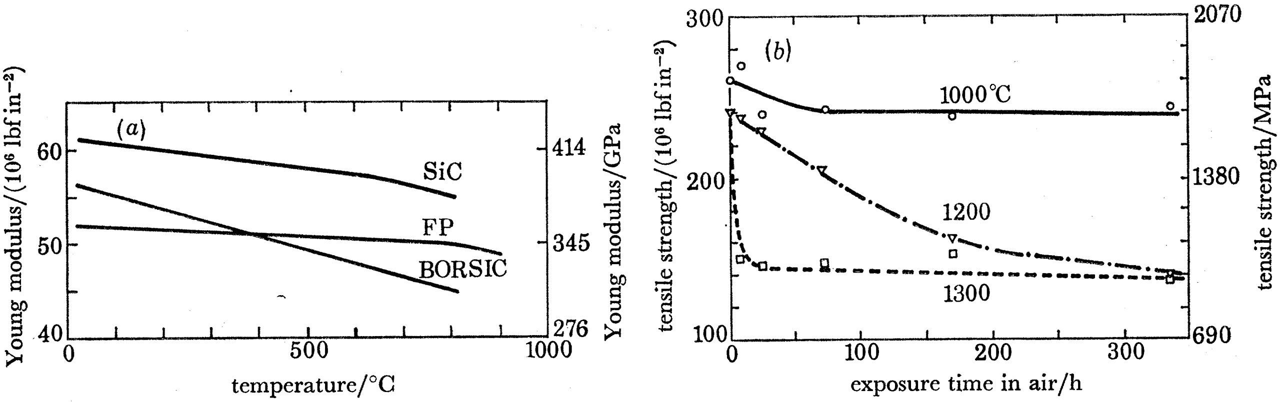

FIGURE 4. (*a*) Young modulus of Fibre FP at high temperatures.
(*b*) High temperature tensile strength of silica coated Fibre FP.

The high temperature behaviour of Fibre FP is depicted in figures 3 and 4. The high temperature strength retention of Fibre FP is shown in comparison with other inorganic fibres, silicon carbide, boron, silicon carbide coated boron, and high temperature metal fibres tungsten and stainless steel in figure 3 (*a*). Fibre FP shows no drop in strength up to 1000 °C, whereas other fibres oxidize and show significant decrease in strength with increasing temperature.

The effect of exposure time in air on the strength of Fibre FP at elevated temperatures is shown in figure 3 (*b*). Fibre FP retains almost 100 % of its room temperature strength after 300 h exposure in air at 1000 °C. Silicon carbide coated boron filaments lose 50 % of their room temperature strength after 1 h exposure at 500 °C in air.

The Young modulus of Fibre FP as a function of temperature is shown in figure 4 (*a*). Fibre FP is essentially unchanged in modulus from room temperature to about 1000 °C. Figure 4 (*b*) shows that silica coated Fibre FP reflecting the inherent refractoriness of α-Al_2O_3 retains useful tensile strength even after 300 h exposure in air at 1300 °C.

MICROSTRUCTURE

The scanning electron micrographs of Fibre FP are shown in figure 5 (plate 1). Figure 5 (*a*) shows typical FP filaments in the yarn. The fractured end of the fibre showing the inorganic brittle nature of the fibre is shown in figure 5 (*b*). The fibre has a rough surface (figure 5 (*c*)) which gives the abrasion resistance and good bonding between the fibre and the matrix. Figure 5 (*d*) shows the polycrystalline grains of the fibre with an average size of about 0.5 μm.

POTENTIAL APPLICATIONS

There are five different composite products based on Fibre FP under development for potential applications. These are composites of Fibre FP and aluminum, magnesium, lead, glass and FP/Kevlar resin hybrids. For the FP/aluminium and FP/magnesium metal matrix composites we see potential applications in aircraft structures, helicopter transmission housings, missile components, ordnance and armour, in the high temperature engine and propulsion systems, and for weight critical transportation systems. We have programmes with the leading aerospace companies and government laboratories to develop the data base and fabrication technology to prove out value-in-use in these applications. For the FP reinforced lead, applications may be in lightweight battery plates and corrosion resistant chemical vessels. FP/resin and FP/Kevlar hybrid resin composites have excellent dielectric, mechanical and radar transparent properties which make them attractive for applications in radar transparent structures in aircraft and missiles, high energy circuit boards and electronic substrates. FP/glass and FP/ceramic composites are prime candidates for high temperature radome applications because of the unique combination of properties including high temperature strengths and stiffness, dielectric properties, erosion resistance and laser hardness.

In the future, if proved cost effective, Fibre FP offers promise for reinforcing aluminium and magnesium castings for weight, wear and temperature critical automotive applications in pistons, gear boxes, push rods, valves and connecting rods. Fibre FP may have the same potential in reinforcing aluminum and magnesium castings as fibreglass did in reinforcing plastics a few decades ago.

Discussion

N. Peacock (*Department of Fibre Science, Strathclyde University, Glasgow, G1 1XW, U.K.*). (*a*) How good is the abrasion resistance of Fibre FP? (*b*) Does Fibre FP abrade other materials seriously? For example, does one have to use special techniques when weaving, in order to prevent excessive wear on yarn guides?

A. K. Dhingra. (*a*) Since Fibre FP is essentially $> 99\,\%$ α-Al_2O_3, it has very good abrasion resistance. Fibre FP reinforced composites have shown excellent abrasion and wear resistance.

(*b*) Special techniques to improve fibre handleability are used to weave FP fabrics. Fibre FP, being a high modulus ceramic fibre, is inherently brittle and difficult to handle. To improve handleability, FP yarn is first coated with a flexible fugitive binder (such as polyethylacrylate) and then overwrapped with a low denier rayon at about 2 wraps/cm before weaving in a loom. Woven fabrics are then heated in air to burn off the fugitive binder and rayon to obtain alumina Fibre FP fabrics. Using this technique, FP fabrics of various constructions including plain and satin weave have been prepared. No wear problems have been encountered in the preparation or use of FP fibres.

A. R. Ubbelohde, F.R.S. (*Imperial College, London, U.K.*). Does the coating of silica used to strengthen the alumina fibre form a discontinuous sleeve, or does its bond-system key into that of the alumina core?

A. K. Dhingra. The nature of the silica coating on Fibre FP is not very clear. We apply a thin coating of silica (about 40–50 Å) on the FP yarn which is fired to optimize strength. Analytical techniques including e.s.c.a. (electron spectrometry for chemical analysis) and s.i.m.s. (secondary ion mass spectrometry) show aluminosilicate widely spread over the fibre surface. The aluminosilicate is perhaps formed by the interaction between the applied silica and the alumina of the base fibre. E.s.c.a. showed that the Si/Al ratio was 1.1–1.7 for the coated fibres compared with 0.04–0.05 for uncoated fibres. S.i.m.s. showed that Si/Al ratio for coated fibres was about 0.4–1.1 in the outermost layer decreasing to 0.22 to 0.74 at the depth of about 20 Å. There appears to be no noticeable visual difference between uncoated and silica coated FP fibres even at high magnifications.

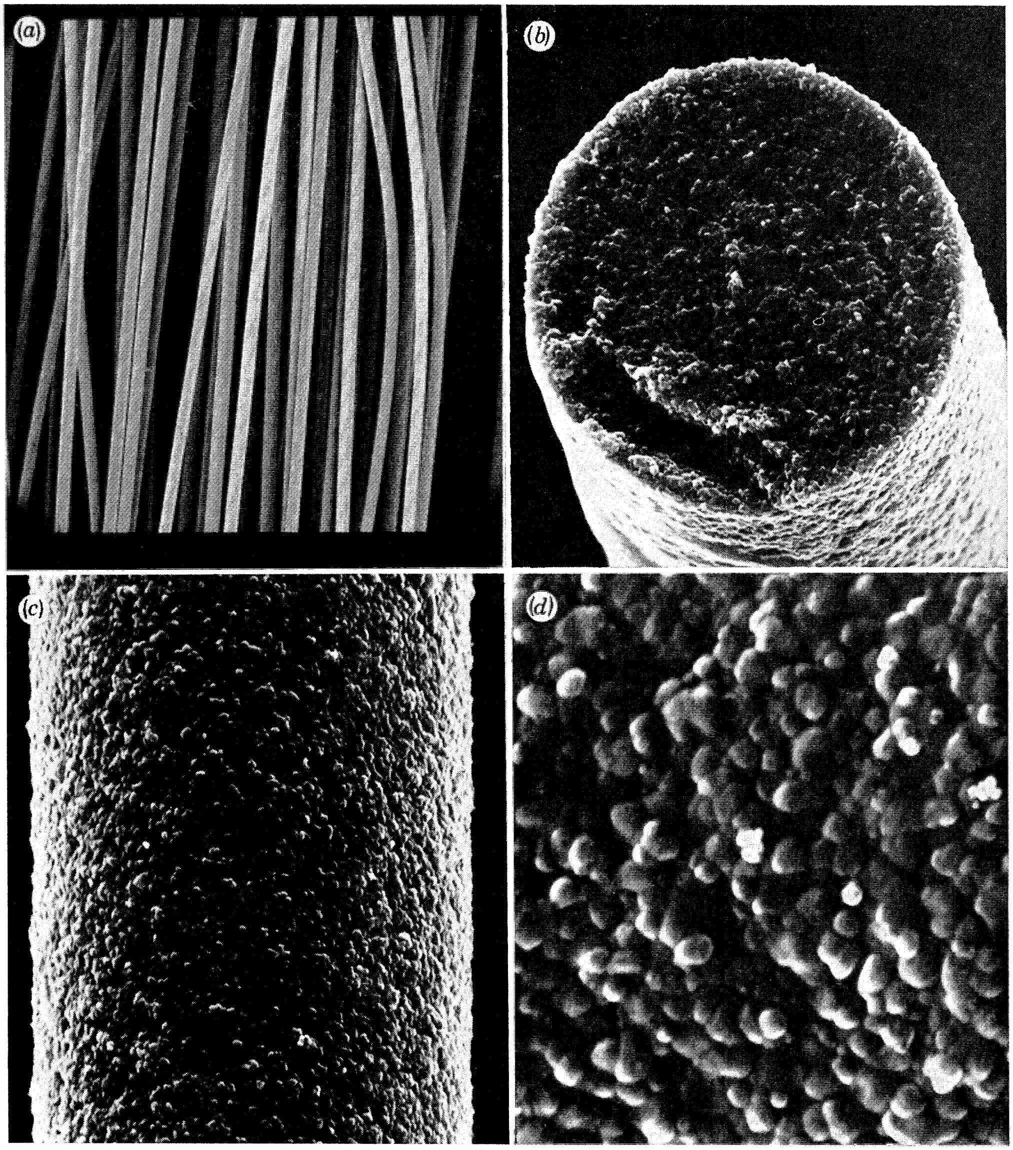

FIGURE 5. Scanning electron micrographs of Fibre FP.
(*a*) Typical FP filaments in the yarn (× 100).
(*b*) Fractured end of the brittle FP filament (× 3000).
(*c*) Fibre FP surface showing roughness useful for fibre–matrix bonding (× 3000).
(*d*) Fibre FP surface showing polycrystalline ceramic grains (× 6000).

C. **Manfre** (*Centro Ricerche Fiat, Orbassano* (*Torino*), *Italy*). It is well known from the basic and practical research that molten metals, including Al and Mg, do not wet alumina at all. So what has been done to make the FP fibres suitable to reinforce Al, Mg and their alloys, especially as the technology to disperse the fibres is the casting method?

A. K. **Dhingra**. Magnesium and magnesium alloys wet alumina Fibre FP (without fibre degradation) forming strong fibre matrix bonding. Magnesium perhaps reduces Al_2O_3 as seen by the greyish colour of the original white FP fibres leached out of the composites by dissolving away the magnesium matrix.

Aluminum and aluminum alloys do not wet Fibre FP. Proper wetting between Fibre FP and aluminum (to prepare FP/Al composites) is achieved by the addition of about 2% lithium to aluminum. Addition of lithium to aluminum forms metallurgical Al/Li alloys which are quite reactive to form chemical bonds with Fibre FP by reducing Al_2O_3, perhaps by the following reactions:

$$6Li + Al_2O_3 \longrightarrow 3Li_2O + 2Al, \quad Li_2O + Al_2O_3 \longrightarrow 2LiAlO_2.$$

Fibre FP (originally white in colour) is found black when leached out of the FP/Al–Li composites by dissolving away the matrix. From X-ray techniques, $LiAlO_2$ has been found on the black fibres. We believe this black colour is caused by defect oxygen-deficient Al_2O_3, which is reoxidized to original white FP fibres when the black fibres are heated in air at about 800 °C.

The wetting between Fibre FP and magnesium or Al/Li alloys is further improved by coating the fibres with a thin layer of silica.

Fibre FP process

- Based on textile fibres spinning technology
- Potentially low cost

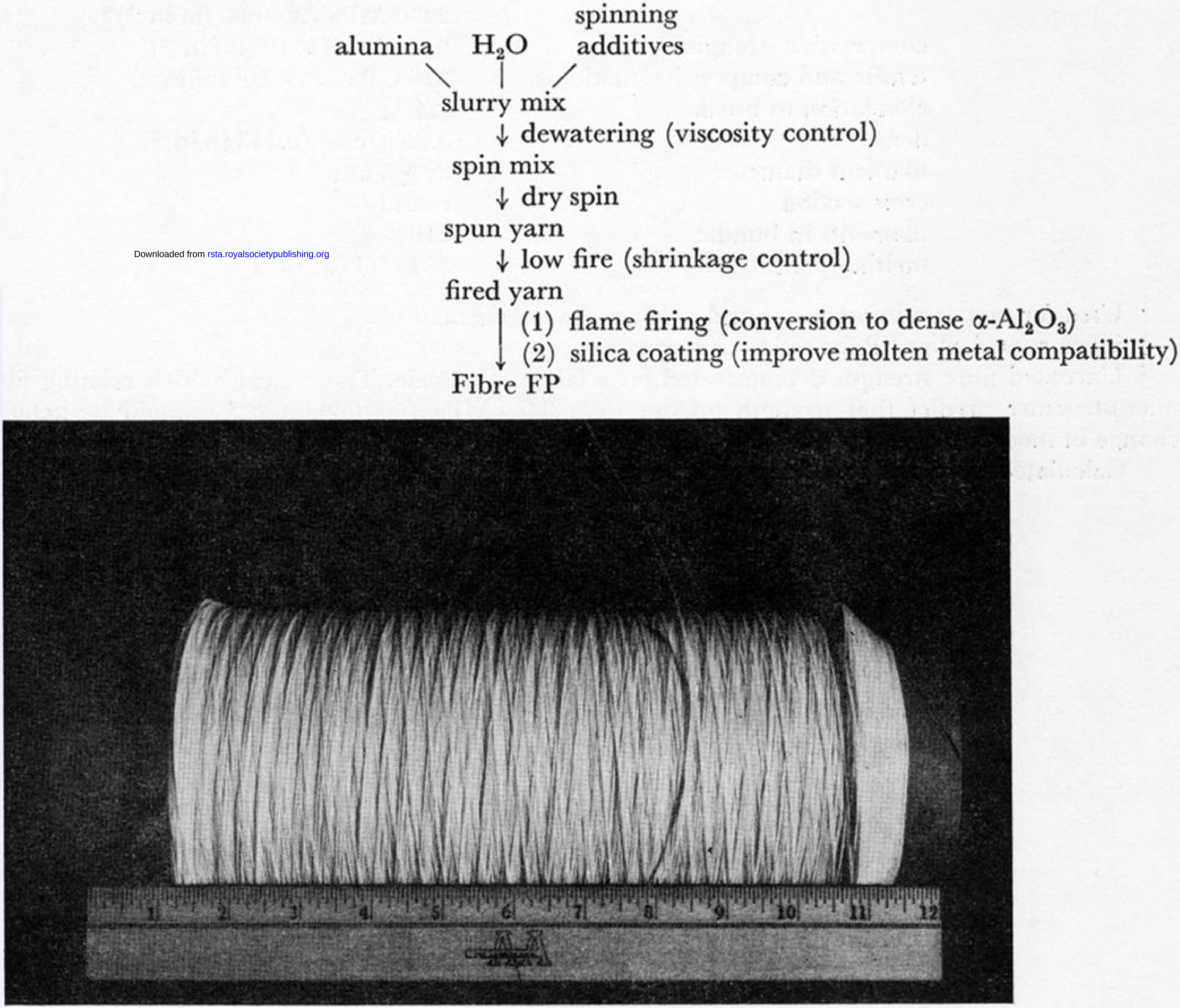

FIGURE 1. Fibre FP process, based on textile fibres spinning technology. This is a potentially low cost process.

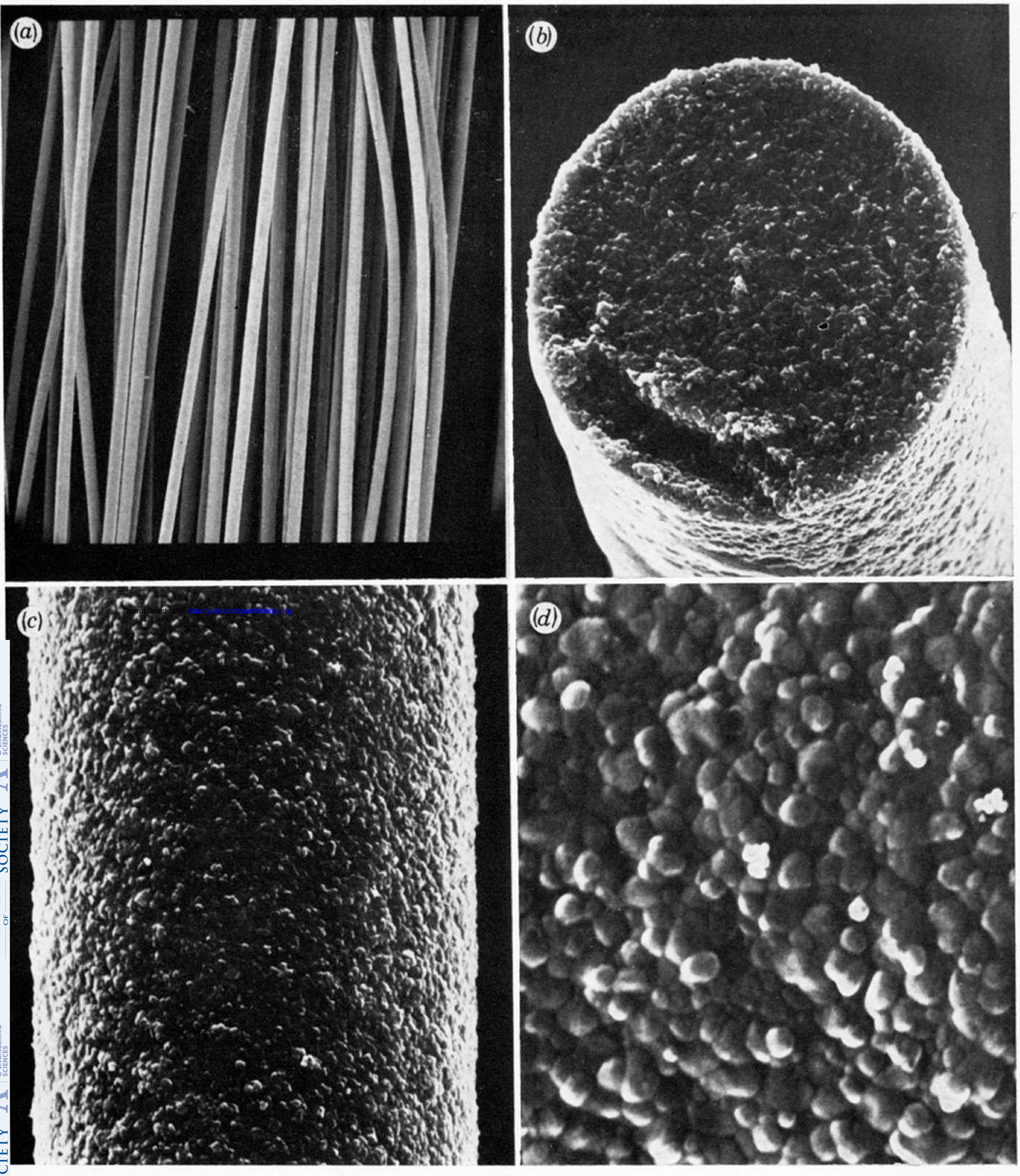

FIGURE 5. Scanning electron micrographs of Fibre FP.

(*a*) Typical FP filaments in the yarn (× 100).
(*b*) Fractured end of the brittle FP filament (× 3000).
(*c*) Fibre FP surface showing roughness useful for fibre–matrix bonding (× 3000).
(*d*) Fibre FP surface showing polycrystalline ceramic grains (× 6000).