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The comparison of alumina and zirconia fibres using simple thermal and mechanical techniques

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The laboratory development of sol/gel ceramic fibres requires rapid objective means of assessing the mechanical and thermal properties of a product at the earliest stages of preparation. The merits of a simple tumbling test, leading to a fibre friability index, and the Bend Stress Relaxation test, which gives a high temperature creep rating, are demonstrated on commercial *Saffil* and *Safimax* alumina fibres and a development *Saffil* zirconia fibre, each in staple blanket form. Measurements on *Altex* continuous alumina/silica fibre and *Nicalon* are also presented.

Standard and off specification alumina fibres are readily distinguished by their friability indices which correlate with the fibre strain to break.

Saffil and *Safimax* alumina are comparable to *Nicalon* in terms of creep and superior to *Altex*. *Saffil* zirconia approaches alumina creep performance after post firing to 1250 °C.

1. Introduction

In previous work we have described the preparation of zirconium titanate [1], mullite [2] and several ferrite [3–5] fibres in a demonstration programme to show how refractory and effect fibres can be made by aqueous sol–gel routes. The fibres are made in a proprietary blow spinning process, which can make precursor fibres from a wide range of inorganic materials. This versatility arises because in blow spinning the draw down forces are applied progressively along the length of the fibres, rather than from a remote point, so that fibres can be made from low viscosity or mechanically weak gel precursors, which would be difficult to spin in a more conventional continuous spinner. A useful feature of the process in the early stages of evaluation is that blow spun fibres are laid flat on the collecting substrates, and the blankets, whether aligned or two-dimensionally random, separate naturally into thin laminations between ten and 50 fibres thick.

The earliest attempts at the preparation of a new ceramic fibre usually lead to a low diameter (3–10 μm) staple product in blanket form. The ultimate ceramic is made by heat treatment of the gel. Fibre properties are definitely a function of the sol precursor and firing regime and are sometimes affected by spinning conditions. Fibres of useful strain to break are essential and are made in an evolutionary experimental programme, which requires the objective comparison of products made with different preparative procedures. The strength and strain to break of the brittle fibrous material is determined by the tiny incidence of flaws, typically between 0.1 and 0.5 μm. These are not easy to detect microscopically, and are not usually simply related to porosity or crystallinity. Tensile strength and modulus must be measured and the conventional method of assessment is too slow at these early evolutionary stages, since it may take a day or more for a dedicated operator to characterize a single fine fibre sample on a microtensile testing machine.

This note shows that a simple friability test would enable a non-specialist operator concerned with process chemistry to make a rapid ranking of the strain to break of a new blow spun fibre. The test was used by 3M [6] in the development of the Nextel range of continuous ceramic fibres and gives sensible results when applied to commercial staple fibres with defined properties.

2. Experimental procedure

High temperature creep behaviour may be sensitive to small changes in formulation and may also be optimized in the early stages of a development. The bend stress relaxation (BSR) technique, developed by Morschner and DiCarlo [7], has been used in another work [8] to rank the creep performance of single continuous fibres and whiskers. Morschner has discussed the theoretical aspects of the technique at some length. This note takes a purely empirical approach in applying the technique successfully to staple fibre blankets.

Staple fibres investigated were Saffil random and Safimax aligned alumina blanket from ICI PLC. These fibres contain 4% silica. Saffil LDM and Safimax SD are sintered and are principally δ- with 7–10% α-alumina. Safimax LD is an aligned porous fibre with the same silica content, crystal phase η-alumina, with a measured 43% porosity and a cumulative surface area of 143 $m^2 g^{-1}$. ICI had made available reject 'flared' Saffil

LDM fibre, which had been weakened by uncontrolled exotherms during heat treatment.

The median diameters of the sintered and porous alumina fibre are 3 and 3.6 μm, respectively. A sample of Saffil zirconia fibre (2.9 μm median), which used to be manufactured in the 1970s and had been fired to 800 °C, was tested. This fibre is partially stabilized with 7% w/w yttria and is reported to be mainly tetragonal with a trace of a second phase. Our measurements showed 21.8% porosity and a cumulative surface area of 18 $m^2\ g^{-1}$. The fibre was post-fired to 1250 °C after initial testing and the porosity reduced to less than 5%. All the staple fibres were of narrow diameter distribution.

Two continuous fibres, Altex and Nicalon, were tested as a check. Sumitomo Altex a 18 μm alumina fibre containing 15% silica has similar tensile properties to the highest quality Nextel type fibres characterized in the 3M's friability test, and its creep behaviour has been reported by Wilson *et al*. [9]. Nicalon silicon carbide fibres (13 μm) have already been tested using the BSR technique [7]. Before testing the continuous fibres were heated to 600 °C in air to remove protective sizes.

In the friability test a sample of fibre is placed in a glass container with rubber stoppers and rotated at a standard speed for 5 min. The residue of fibre retained on a standard sieve is then determined; the friability index being the fraction of fibres retained. The technique was modified slightly to use the nearest European jar (0.5 l) and 28 stoppers of 11 mm diameter and a total weight of 118 g. The jar was rotated for the same speed (155–160 r.p.m.) and time (5 min), and the sieve size (840 μm) and sample size (0.2 $\pm$ 0.05 g) were the same. There were other minor modifications compared with the 3M fibres, and stoppers were washed on to the screen rather than tumbled dry; subsequent washing was done with water and a 1% solution of ICI Hypermer C-6 rather than with a simple detergent. A final modification was that retained fibres were washed on to a filter paper, dried and weighed.

3. Results and discussion

Table I shows measurements of the friability indices. That of Altex is high, and the shortfall, 0.95 rather than 1, probably reflects small losses brought about by modifications to the technique. Saffil LDM produced on a BS5750 controlled manufacturing unit is better than Safimax SD, and both rank well above the reject 'flared' Saffil LDM.

The zero index of Safimax LD was unexpected, as the sample was subjectively very strong in tension, and in this case the pore structure [10] suggested a good tensile strength. Saffil zirconia scores low, but the indices for all materials correlate well with measurements of strain to break made by wire indentation. The lower resistance of the random Saffil LDM to wire indentation compared with Safimax SD is probably due to breakage at the points of fibre cross over.

Wire indentation tests were done by gluing a thin strip of fibres on to the surface of transparent double-sided adhesive tape, which in turn was glued to a soft rubber pad. The wires were held in toolmakers' clamps and pressed into the sample. The rubber was then peeled from the tape and the fibres examined for lines of breakage using a low power $\times 40$ optical microscope. The technique is useful for correlation, but is not preferred in routine work because the wires stretch and break too easily.

TABLE I Friability test results

Fibre	Strain to break[a] (%)	Friability[a]	Strain to break[b] (%)	Gauge length[b] (mm)
Safimax SD	0.85–1	0.44	0.7	1
Safimax LD	<0.3	0	≤1	1
Saffil LDM	0.65–0.9	0.52, 0.67, 0.68	0.7	1
Saffil CG	<0.3	0.05	—	—
Flared Saffil	0.4–0.5	0.2	—	—
Saffil zirconia	0.5	0.26	—	—
Post-fired	0.5	0.28	—	—
Altex	1.6–1.8	0.95	1	25

[a]Test results.
[b]Manufactures' data.

The BSR technique was used to compare the creep performance of the different fibres in air. Alumina rods of 2.1, 3.9, 5.5 and 8 mm diameter were used as bending jigs. Laminations from the staple blankets were cut into strips 0.5–1 mm wide by 5 mm, and these or individual fibres were bent around a rod and held at temperature for 1 h. If the sample has remained elastic it straightens fully when removed from the jig, while a fully relaxed sample takes up the radius of the rod. For intermediate cases we have ranked the creep performance with the parameter, $m = (1 - R_o/R)$, where R_o is the radius of the rod and R the curvature taken up by the fibre.

Measurement of R is done with an outside radius drawing template, circles being available at 1/64 inch intervals from 1/32 to 3/32 then at 1/32 intervals up to 0.5 inches. The circles are easily matched to the inside arc of the laminate strips after relaxation, the early intervals of 1/64 inch giving sufficient definition for this work. It was proposed initially to measure the radii microscopically, but the laminates became twisted when transferring to a slide and the twisting reduces the projected radius very significantly.

The staple fibres were usually tested with the 2.1 mm rod. There was no systematic effect of rod diameter between 2.1 and 8-mm when checked with Safimax SD at 1100 °C as shown in Fig. 1, although the data are scattered as m is changing rapidly at this temperature.

Overall creep data are shown in Fig. 2. There is a degree of scatter in points measured at a fixed temperature and this is seen in the data of other workers. In spite of the scatter, the generally steep fall in m over a narrow range of temperatures enables us to distinguish between the different fibres. Safimax SD and Saffil LDM are indistinguishable with relaxation data similar to that reported by King and Halloran [8] for fibre PRD and better than Altex. The as-received zirconia and Safimax LD, both porous fibres, creep appreciably at lower temperatures, while post-firing the zirconia to 1250 °C brings the performance closer to the alumina-based materials.

Nicalon is scarcely better than the sintered alumina-based fibres in this test, and inferior to the performance reported by Morschner and DiCarlo [7] ($m = 0$

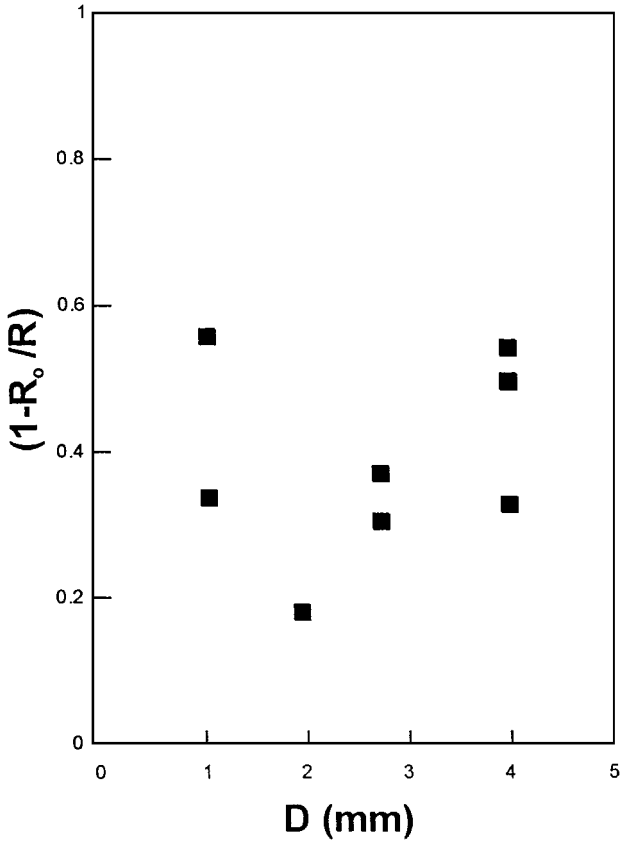

Figure 1 Variation of relaxation parameter, $1 - R_o/R$, with jig rod diameter, D.

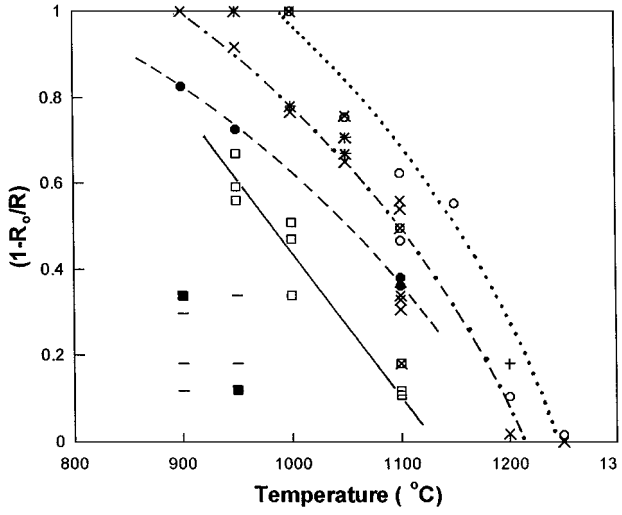

Figure 2 Relative creep relaxation for commercial ceramic fibres: (·—×·—) Safimax SD, (+) Saffil LDM, (···O···) Nicalon, (■) Saffil Zirconia, (—□—) Saffil Zirconia (post-fired), (—) Safimax LD, (– –●– –) Altex.

at 1250 °C rather than 1400 °C). The accuracy of radius measurement becomes critical at small values of m and their measurements are more accurate than those possible with a template. Nevertheless the difference between their results and those presented here should be detectable and it is possible that there are real differences between the Nicalon tested by Morschner and DiCarlo and the present sample, which was procured in 1987.

4. Conclusions

The crystals of α-alumina in the Saffil LDM and Safimax SD fibres are platy and extend across the fibre diameter, an unusual structure that may account for their relatively good creep behaviour.

The staple fibres tested in this work have been proven over a range of applications, so that an assessment of the ultimate utility of an experimental product can be made at an early stage of development. The zirconia fibres have been used in the fabrication of electrolytic cell diaphragms, so that even a moderate friability index of 0.25 will not exclude a new fibre from all applications.

Fibre friability involves factors other than strain to break. Studies on carbon and glass fibres have shown that resistance to abrasion decreases as the diameter falls below about 6–8 μm [11], so that other things being equal we should expect a lower index from the finer staple fibres.

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