Critical requirements in the formation of continuous ceramic fibre precursors

D V Varaprasad, Bruce Wade, N Venkatassubramanian, Prashant Desai & A S Abhiraman
Polymer Education & Research Center, Georgia Institute of Technology, Atlanta, GA 30332, USA
Received 3 December 1990

The formation of ceramic fibres from organometallic precursors has been discussed. Critical requirements in precursor polymerization and fibre formation by sol-gel spinning have been highlighted. Silicon alkoxide precursors have been used to study spinable sols. The influence of stress, environment and temperature-controlled rates of conversion of the precursor fibres on structure and properties of ceramic fibres has been demonstrated. It has been concluded that a broad range of ceramic fibres can be tailored through appropriate precursor synthesis, fibre formation routes and subsequent conversion to the desired ceramic structures for composites.

Keywords: Ceramic fibres, Polycarbosilane, Precursor polymerization, Silicon alkoxide precursor, Sol-gel spinning, Thermal consolidation

1 Introduction

The development of high performance refractory fibre forming materials is amongst the most important recent advances in materials engineering. A broad range of materials, covering a spectrum of unique physical and mechanical properties, is being developed to meet a variety of highly specialized needs. Significant among these are carbon fibres from organic precursor polymers and ceramic fibres from polymeric precursors. We have the potential with such materials for developing fibrous structures with many combinations of superior physical properties, such as high stiffness and strength, low density, high temperature performance, unique electrical properties and interaction with electromagnetic radiation. Of particular importance in the development of high temperature structure composites are the ceramic reinforcement fibre structures, such as Si$_3$N$_4$, SiC, BN, and oxides and mixed oxides of aluminium, silicon, titanium and zirconium. These and other potential applications have motivated considerable expansion of research in synthesis and processing of a variety of new materials (Table 1) including superconducting mixed oxides.

Critical reviews pertaining to the formation of these ceramic structures through polymer pyrolysis or sol-gel transitions, followed by high temperature consolidation, have been published. Much of the anticipated developments in this regard are predicted on advances in precursor materials and processes for the formation of appropriate filamentary structures.

Rapid and successful development of a range of precursor materials and their chemical/physical

| Table 1—Ceramic fibres derived from polymeric precursors |
|-----------------|-----------------|
| **Oxide Sol-Gel** |
| **Glass fibres** |
| SiO$_2$, SiO$_2$-Al$_2$O$_3$, SiO$_2$-TiO$_2$, SiO$_2$-ZrO$_2$, SiO$_2$-ZrO$_2$-Na$_2$O |
| **Polycrystalline fibres** |
| $\eta$-Al$_2$O$_3$, Al$_2$O$_3$-B$_2$O$_3$, Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$, TiO$_2$-ZrO$_2$, ZrO$_2$-CaO, Al$_2$O$_3$-Cr$_2$O$_3$-Mo$_2$O$_3$ (where $\eta$ = Si, Ti, Zr or Sn); Al$_2$O$_3$-SiO$_2$ and optionally P$_2$O$_5$, B$_2$O$_3$ or Cr$_2$O$_3$; Superconducting YBa$_2$Cu$_3$O$_{x}$, and Bi-(Pb)-Sr-Ca-Cu-O |
| **Non-oxide Ceramics** |
| Precursor | Ceramic fibre |
| Polysilazanes | SiC-Si$_3$N$_4$ |
| Polycarbosilane | SiC |
| Polysilastrene | SiC |
| Polyisotitanocarbosilane | Si$_3$Ti$_2$C$_4$O |
| Polysilazane | Si$_3$N$_4$C$_3$ |
| Methylchloropolsilazane | SiC |
| Polydisilazanes | SiC(Si$_3$N$_4$) |
| Polycarbosilane | Si-N-O |
| Polycarbosilane | Si$_3$N$_4$ |
| Poly(decaborane-diamine) | BN |
| Polyborazines | BN |
| Polyborates | BN |

*To whom all correspondence should be addressed.*
conversion to the desired high temperature filamentary materials require the combination of a comprehensive range of research facilities and experience, ranging from synthesis of polymers, through fibre formation, to conversion of precursor fibres in controlled continuous thermo-mechanical processes to high performance fibres. Its absence can lead to a higher than necessary level of empiricism and guess-work, and shot-in-the-dark approaches in material and process development.

In analogy with the highly successful development of carbon fibres, ceramic fibres from polymer precursor materials also require chemical conversion/consolidation of appropriately formed precursor fibres. However, the chemical path to most of these ceramic fibres also requires the development of precursor fibre formation routes which would allow simultaneous evolution in the chemical structure. We present in the following a summary of the critical requirements which exist in each of the three mutually dependent stages for successful development of ceramic filaments from polymeric materials, viz. precursor synthesis, formation of precursor polymer fibres and thermal conversion/consolidation. The major emphasis in this discussion is on the expertise in precursor fibre formation which traditional fibre scientists could bring to this research effort.

2 Precursor Polymer Synthesis

(Controlled synthesis of precursor polymer with the potential for yielding fluids of spinnable rheological characteristics and rapid transformations to a gel or solid-like state, which can be subsequently converted cohesively to the desired ceramic structure)

The emphasis here should be on determining the most appropriate precursor and the optimum conditions for the production of the precursor materials from known as well as new synthetic routes. In cases where more than one precursor polymer or more than one path for its synthesis may exist, the choice may be based on the following set of criteria.

(i) Ability to generate reproducibly spinnable compositions that can yield precursor fibres suitable for subsequent conversion processes.
(ii) The range of structures and properties of the high performance refractory fibres that can be obtained.
(iii) Process and product quality that can be achieved, especially with respect to the degree of tolerance to minor variations in materials and process parameters.
(iv) Economic evaluation which would include, besides material and processing costs, consideration of the required processing systems in relation to currently available processing facilities in the industry.

The options that can exist at the precursor stage are well exemplified by the different synthetic routes which have been developed for the formation of SiC, Si₃N₄ and oxides and mixed oxides of silicon and zirconium⁶,13,17,27. For example, silicon carbide fibres can be obtained by any of the following routes.

(i) Reaction of dimethylchlorosilane with metallic sodium to form insoluble poly(dimethylsilane), which on high temperature and high pressure treatment yields polycarbo silane. The non-volatile and hexane-soluble fraction can be melt spun, stabilized through air oxidation and then converted at high temperature cohesively to silicon carbide fibres⁸.
(ii) Poly(dimethylsilane) can be converted to polycarbo silane at high temperature and ambient pressure through the addition of borodiphenylsiloxane⁹,10.
(iii) Reaction of dimethylchlorosilane with phenylmethyldichlorosilane in the presence of sodium metal yields a polysilane copolymer. This copolymer can be melted and it is also soluble in common organic solvents⁶. Fibres of this copolymer can be rendered insusible through crosslinking with UV radiation and then converted to SiC at high temperatures in an inert atmosphere³¹.

A comparative experimental study of these and other options in the context of the complete fibre formation process and the structure and properties of the product is essential for developing the most appropriate route for the production of SiC fibres. The predominant tendency in exploring (synthesizing) precursor materials for such fibres has been to seek melt-processible precursors, motivated primarily by perceived ease of processing with melts and concern regarding unconsolidated (porous) structures which might arise from solution processing. It is possible that a number of otherwise promising precursors, e.g. materials which might provide better stoichiometric balance of the desired elements in the final ceramic structure, have been neglected due to their insusible nature which would exclude melt processing. These concerns are essentially unwarranted. Well densified precursor filament structures can be produced by solution-based routes. For example, Fig. 1 shows an experimental polycarbo silane filament drawn from a solution in heptane and dried in air. It can be seen clearly that a well densified precursor fibre is obtained

---

⁸Which may offer the option of melt-solution (wet or dry) spinning.
by this route. The FTIR spectrum of the dried fibres obtained from solution spinning (Fig. 2) is characteristic of the precursor polymer. Comparing the thermogravimetric response of bulk polycarbosilane precursor with its solution in heptane (Fig. 3) also shows that any concern regarding the influence of solvent on thermal conversion of this precursor is unwarranted. Solution-based routes also offer the possibility of using a low concentration of soluble polymeric rheological aids which would be fugitive during subsequent consolidation.

Another example of the choices offered can be seen with currently explored precursors for boron nitride fibres. Fibres of boron nitride, if they can be obtained in hexagonal crystalline polymorph with the basal planes highly oriented along the fibre direction, would possess mechanical properties comparable to graphite fibres and superior thermo-chemical
Fig. 2—FTIR spectrum of dried polycarbosilane fibres obtained by solution spinning.

Fig. 3—Thermogravimetric analysis of polycarbosilane in argon at 5°C/min to 200°C followed by 10°C/min up to 1200°C: (a) polycarbosilane powder, and (b) solution of 72 wt% polycarbosilane in heptane. Weight loss computed on the weight of the polycarbosilane: (a) 37%, and (b) 32%.

resistance to degradation of those properties. Thus, the requirement that the precursor material for BN fibres should be amenable to being processed into an oriented morphology has to be included along with other criteria. Polyborazines, poly(vinylborazines), poly(decaborane-diamine) and polyborates are among the precursors being explored for this purpose in various laboratories. BN fibres have been produced by nitriding melt-spun boron oxide at high temperatures (200-800°C) in an ammonia environment. These fibres are, however, isotropic and lacking in mechanical properties, unless they can be drawn effectively at very high temperatures (1800-2100°C in nitrogen), which is difficult to accomplish in practice. The low diffusion rates of ammonia in the dense boron oxide precursor and the outer BN sheath also present the problem of long nitridation times to achieve close to full conversion to boron nitride. An alternative route which is currently being explored consists of a porous polyborate precursor fibre which can be formed by sol-gel chemistry beginning with trimethoxyboroxine and boric acid.

Earlier paths to polyborate had consisted of routes which involved either the reaction of cyclohexanol with boric acid or boron oxide with the removal of water as an azo trope with toluene or xylene or hydrolysis and polycondensation of boron alkoxides in the presence of alkali metal alkoxides whereby the metal becomes a counterion to the tetracoordinate boron in the polyborate structure. It is possible...
to form polyborate gel fibres through these routes. For example, a porous polyborate gel fibre could be drawn from this precursor (Fig. 5). Presence of the Li$^+$ counterion in the structure is, however, undesirable for conversion to BN. Concern over the presence of residual organics, such as toluene or xylene, which might lead to excessive carbon upon thermo-chemical conversion, or metal ions which may be difficult to remove from polyborate precursors, has motivated the development of more direct routes. We have shown that it is possible to produce a polyborate sol without incorporating a counterion by a direct polycondensation of trimethoxyboroxine and boric acid. Spinnability of this sol can be improved significantly, as in the case of poly carbosilanes, with a low concentration of a high molecular weight polymer as a rheological aid which is fugitive during thermo-chemical conversion. It remains to be seen if dense and oriented BN filaments can be produced by drawing the porous polyborate filaments during nitriding.

Among the boron-nitrogen precursors which are being explored currently as precursors for boron nitride, viz. polyborazines, poly(vinylborazines) and poly(decaborane-diamine) structures, only the unsubstituted polyborazine (polyborazylene) appears to offer a reasonable scheme for producing oriented BN through precursor orientation. It should be noted that all of these precursors for BN require almost prohibitively expensive starting materials.

Routes which involve a sol-gel transition present an interesting challenge because of apparently conflicting requirements in polymerization and fibre formation. The key to successful integration of the chemistry of sol-gel processes, e.g. in the formation of metal oxides from multifunctional precursor monomers, with possible routes for continuous fibre formation and subsequent thermo-chemical consolidation, lies in meeting the combination of "hydrolysis and polycondensation of the multifunctional monomer to yield a stable, spinable fluid" which would be, nevertheless, "cohesively unstable, i.e. gel rapidly and cohesively, in continuous filament extrusion". Simple mechanisms for meeting these requirements will be exemplified in the following section.

The preceding examples have been offered to stress the importance of a broad-based research effort in the general context of the formation of ceramic fibres from polymer precursors, most of which offer more than a single synthetic route.

### 3 Formation of Precursor Polymer Fibres

(Identification and development of fibre formation routes tailored for the specific precursor material on hand)

A variety of options exists for the formation of fibrous structures, namely melt spinning, solution-wet spinning, solution-dry spinning, dry-jet wet-spinning, sol-gel spinning, phase separation spinning, vapour phase growth of filaments, etc. along with a number of post-spinning thermo-mechanical operations such as plastic drawing, plasticized drawing, thermal annealing, etc. It is necessary at this stage to identify the viable options for a particular precursor material and also to provide the directions necessary for the synthesis of a spinable precursor.

With the notable exceptions of certain processes for forming SiC, Si-C-N, silica and alumina fibres which are currently in either commercial or pilot-scale production, the development of a majority of ceramic fibre structures which can be obtained from polymer precursors is at its early stages. Even with regard to the exceptions cited here, it is widely accepted that much improvement can be achieved in both process quality and the properties of the fibres produced. The need here is to design the most appropriate system of fibre formation corresponding to each precursor material and also to detail the effect of critical process parameters on the structure and properties of precursors as well as the ultimate ceramic fibre structures. In particular, the range of structures that can be obtained at different rates and extents of extensional deformation in the fluid-like state, rates of transition from the fluid to the gel or solid-like state, and any possible (and necessary) deformation subsequent to coagulation gel formation solidification should be explored in detail.

The mutually dependent requirements in precursor polymerization and fibre formation are
best exemplified by hydrolysis and polycondensation of metal alkoxides, e.g. silicon alkoxides, to form spinnable sols (Fig. 6) followed by fibre extrusion, with the sol-gel transition effecting transformation of the fluid threadline to a solid-like gel filament. Recent research in several laboratories\textsuperscript{1,4,5,7-67}, including ours, has addressed these issues. The initial emphasis of our studies in this regard was on generating stable spinable solutions, with rheological characteristics that would be suitable for incorporation into a continuous fibre spinning process.

Silicon alkoxide precursors such as tetraethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS) and ethyl silicate-40 have been used to study spinable sols in our laboratories. Hydrolysis and polycondensation have been carried out through dropwise addition of water, containing an acid catalyst (HCl), to an ethanolic solution of the alkoxide, followed by exposure of the prepared solution to a humid atmosphere to enhance the reactions. Consequences of the course of reactions have been monitored through rheological
characterization as a function of reaction time, temperature and concentration of reaction species. The range of combinations of these factors that is essential for generating fluids with spinnable rheological characteristics (high spinnability ratio in dry spinning/cohesive coagulation in wet spinning) which would also be stable for extended periods when cooled to low temperatures (constant rheological characteristics over a period of days) has been identified. An example in this regard is given in Table 2. This experience has shown that (i) it is almost a trivial exercise to obtain fiberizable solutions in the sense in which it has been widely reported in the literature, and (ii) the combined requirements of continuously spinnable rheological characteristics and stability of composition and physical structure of the fluids can be met only through a very careful study of the factors which have been identified.

Many of the precursor polymers can be converted to continuous filaments by more than one method. For example, in the sol-gel spinning through hydrolysis and condensation reactions of TEOs, analogues of conventional wet and dry spinning process schemes can be used to effect the removal of solvent and promote crosslinking reactions. In each case, the extent and the rate of deformation can be changed by the appropriate choice of temperatures, residence times and the composition of the reaction environment (reaction liquid bath or vapour environment), leading to a wide range of physical structures and mechanical properties.

An important issue in the formation of precursor fibres by the sol-gel route arises from the apparently conflicting requirements of a precursor spinning solution that would be stable for extended periods before fibre formation, which, nevertheless, can undergo the sol-gel transition rapidly in the filament extrusion process (of the order of 0.1 s in dry spinning and 1 s in wet spinning). It is also necessary for the latter process to occur without generating high internal stresses so that the precursor fibres would have the cohesion necessary for subsequent high temperature consolidation. Examples of conditions which can be used in this regard are given in Figs 7, 8 and 9. An interesting aspect of solution-wet spinning is the catalyst (an amidated polyanine) which has been identified for incorporation in the coagulation (gelation) medium surrounding the filaments in fibre spinning to effect rapid but cohesive gelation of the filament surface.

A fundamental difference exists between the formation of precursor fibre structures through the sol-gel transition and other conventional fibre formation processes which can be used with precursors for materials such as carbon and silicon carbide. The latter involves at the precursor spinning stage only physical transitions such as vitrification, crystallization or coagulation to effect the necessary fluid→solid transformation, whereas the sol-gel

---

Table 2 – Example of a spinnable silica sol

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂O][TEOS]</td>
<td>1.6</td>
</tr>
<tr>
<td>[HCl][TEOS]</td>
<td>0.02</td>
</tr>
<tr>
<td>[C₂H₅OH][TEOS]</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Aging time (h) | 70            |
| Aging temperature (°C) | 70            |
| Viscosity at 25°C (poise) | 260⁰         |

*Stable when stored in a closed container below 0°C.

---

*Much of the research reported in the literature has dealt essentially with the ability to "draw" a filament by dipping a rod into the reaction mixture and pulling it out.

---

Fig. 6—Primary silica sol-gel reactions

Fig. 7—Example of solution-dry spinning [Typical conditions: H₂O:TEOS (1.6:1); HCl catalyst; Viscosity of sol, 270 poise at 20°C]
in winding and subsequent processing of the spun fibre.

(vii) Winding mechanisms.

4 Thermal Conversion/Consolidation
(Thermochemical treatments of the precursor fibres for controlled chemical conversion and consolidation to yield the desired high performance material)

It is necessary to have carefully controlled temperature and stress/deformation profiles, and environments in these thermal treatment processes. When the temperature of a precursor polymer fibre is raised, significant physical relaxations in the internal structure often precede the onset of reactions associated with curing (stabilization) and/or conversion to the ceramic structure. The stresses imposed in these processes can affect the morphological changes resulting from such relaxation phenomena. Also, significant internal stresses can develop as a result of the chemical/physical transformations during thermal treatment. Knowledge of the influence of stress, environment and temperature-controlled rates of conversion on the structure and properties of the ceramic fibres is necessary to establish the optimum conditions for continuous conversion to high performance ceramic fibres. Multi-stage conversion processes are often necessary to obtain the appropriate independent control of the process parameters at each stage. It is especially important to control the time- and temperature-dependent transformations during high temperature conversion of the precursor fibres and their subsequent cooling to room temperature.

5 Remarks

In spite of the recent growth in research on the chemistry of precursor materials for ceramic structures, critical issues pertaining to continuous fibre formation and physical/chemical structures of the fibres remain largely unexplored. These are related to the chemistry of formation and spinnability of precursor materials, stability of precursor fluids, choice of precursor fibre formation routes, and effects of stress fields and environments during fibre formation and subsequent conversion to the desired ceramic structures. Fundamental studies of these aspects are necessary to build a base on which a broad range of fibrous structures can be developed most efficiently. Bringing together appropriate expertise in materials synthesis, process engineering and material structures is essential in developing the required fundamental knowledge to effect a significant growth in the exciting field of ceramic fibre science and technology.
Acknowledgement

The authors acknowledge gratefully the support for this research provided by the US Office of Naval Research-Chemistry Division and PPG Industries.

References

