All-Oxide Ceramic Matrix Composites

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by

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October 2001
to my father Rolf

Science tells us what we can know,
but what we can know is little,
and if we forget how much we cannot know
we become insensitive to many things
of very great importance.

Bertrand Russell (1872-1970)

"The scientific theory I like best is that the rings of Saturn
are composed entirely of lost airline luggage."

Mark Russell
Preface

The work presented in this thesis has been carried out at the Division of Engineering Materials, Luleå University of Technology, Sweden, during 1995-2001. It has been mainly funded by the Swedish Research Council for Engineering Sciences (TFR). One part of the work has been performed within a Brite-Euram project (project number BE-1598-UHT CMC). The last part of the work was performed at Oak Ridge National Laboratory in Tennessee, USA, which resulted in three publications (Paper III, IV and V).

The thesis contains an introduction and the following papers

Paper I

Paper II

Paper III

Paper IV

Paper V

Paper VI
M-L. Antti, M. Holmquist, D. LePagne and R. Warren; “Mechanical Behaviour of Long Sapphire Fibre / Alumina Matrix Composites”, to be submitted

Part of the content in Paper VI has been presented at the following conference:


That conference proceeding is not included in the thesis.

Luleå, October 2001

Marta-Lena Antti
Abstract

One of the main problems of stability of materials at high temperatures is oxidation, which can lead to degradation through a variety of processes. One way to overcome this problem is to use ceramic oxides which are inherently oxidation resistant. The brittleness that comes with a ceramic monolithic material due to the strong covalent bonds can be overcome by reinforcement with long fibres. A combination of mechanisms, such as crack deflection and fibre pull-out, lead to a pseudo-ductile behaviour. The crack deflection mechanism in long fibre composites has traditionally been promoted by the introduction of a third constituent, a so called interphase between the fibre and the matrix. A more recent concept uses the matrix as a crack deflection path by introducing a fine scale porosity. In this case there is no need of an interfacial layer, which makes processing easier and reduces the cost.

This thesis covers a number of aspects of long fibre reinforced all-oxide composites including the properties of candidate oxide constituents, methods of composite preparation, microstructure and mechanical properties. The first paper describes attempts made to produce alumina composites reinforced with monocrystalline (sapphire) fibres using hot isostatic pressing. The second paper reports on the thermal expansion behaviour of candidate oxides and the consequences of differences in thermal expansion of composite constituents with respect to residual thermal stresses in the composite. Paper VI reports measurements made of the stress-strain and fracture behaviour of experimental sapphire fibre/alumina matrix composites. The materials studied included both unidirectional and 0/90° cross-ply composites, all with a thin layer of zirconia at the fibre/matrix interface designed to adjust the interfacial properties to provide optimum composite stress-strain behaviour. The results could be linked to measurements made of interfacial properties.

Papers III, IV and V concern the stress-strain behaviour of a commercial all-oxide composite consisting of fine-diameter, polycrystalline oxide fibres in a porous, aluminosilicate matrix. In these composites the fibres were woven in a 0/90° geometry and tested in both the 0/90° and ±45° orientation. The emphasis of the study was on the notch-sensitivity of test specimens containing a central circular hole. Aspects studied included failure mechanisms, the effects of notch size and the effects of high temperature thermal exposure on microstructure and strength degradation. The observed behaviour could be described successfully in terms of a simple model based on fracture mechanics.
Acknowledgements

My sincere thanks go to my supervisor Professor Richard Warren, who has my deepest respect for his great skills in the field of composite materials. I am thankful for having had the opportunity to work with him for these years and for getting the chance to learn from a person who never lacks the answers.

Financial support for a major part of the project from the Swedish Research Council for Engineering Sciences (TFR) is acknowledged. The Royal Swedish Academy of Engineering Sciences (IVA) is acknowledged for not only one, but two scholarships making it possible for me to spend time at Oak Ridge National Laboratory, USA. Seth M. Kempes- and Wallenbergs foundations are also acknowledged for financial support.

I am grateful to Dr Edgar Lara-Curzio of the Oak Ridge National Laboratory in Tennessee, USA, for supervising me during my 4 months stay at the laboratory. He showed me how mechanical testing should really be performed, and how a professional works in a laboratory. My stay at ORNL was also great fun thanks not only to Edgar, but also to my friends and colleagues Laura, Venu, Randy, Doroteo, Vince, Allessandro and Kjersti. The Carlson family in Oak Ridge was a major reason that not only I but also my family had such a great time there.

I would like to thank Magnus Holmquist for a very fruitful collaboration. Thanks for your hospitality and your large energy in discussing mechanical properties of ceramic matrix composites.

My colleagues at the Department of Materials and Manufacturing Engineering are greatly acknowledged for making the department such a nice place to work at. A special thanks to Johnny Grahn and Lars Frisk for all their help in the lab and with computers.

Participating in the Graduate School for Women at Luleå University of Technology has been a great source of joy and encouragement. I would like to thank all my friends there for all the laughs and all the serious discussions we have had. It has been an extremely valuable encouragement especially during times when the mood and self-confidence were low. A special thanks to Lena Trojer for being such a good project leader of the Graduate School.

Friends and colleagues who have meant something extra for me are Maggan, Eva and Elisabeth. An extra hug to Maggan for all practical help with finishing the thesis and for all good advice on all kinds of subjects. Dr Barbara Shollock is thanked for her invaluable encouragement and her friendship.

My parents, Rolf and Judit and my parents in law, Berit and Ragnar are sent a big THANK YOU for help with childcare when needed the most.

Finally, I would like to thank my husband Johan for always supporting and encouraging me during these years and my sons Erik and Albin for all their love.
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1 INTRODUCTION

Research is currently in progress to find better materials that can stand higher temperatures and lead to higher performance in, for example, turbine engines. Ceramic materials have been identified as a promising group due to their chemical stability and high performance up to elevated temperatures. The main obstacle beside chemical stability of a structural component at high temperatures is creep deformation. Ceramic matrix composites reinforced with long fibres are among the most creep-resistant structural materials available and they are considered to be promising candidates for long-term use at elevated temperature. An additional benefit of long fibre reinforcement is that with appropriate adjustment of the fibre/matrix interface, a composite can exhibit non-brittle behaviour and damage tolerance. Most high-temperature materials available today suffer from more or less severe oxidation at temperatures above 1000°C. All-oxide composites, being inherently oxidation resistant are an exception to this. Another requirement is that the components of a composite are chemically and thermomechanically compatible. This requirement severely reduces the number of candidate materials that can be combined in a composite. When considering possible constituents for all-oxide composites to satisfy these many requirements it is clearly of importance to have knowledge of the properties of oxides.

The present work consists of two main investigations. Firstly, two alternative methods of producing fibre reinforced oxide/oxide composites were explored. These involve the coating or cladding of single large diameter fibres to provide a means of producing composites with other than planar geometries, for example, cylindrical test specimens for mechanical testing.

The second aspect of the work was a study of the mechanical properties of fibre reinforced all-oxide composites. The material studied included alumina reinforced with a large diameter sapphire fibre and a commercial composite with a fine-diameter woven fibre reinforcement.

First, in Chapter 2 a general background to ceramic materials and composites is presented. Chapter 3 deals with oxides in general and in particular those that are of interest in matrices and fibres. Chapter 4 describes the experimental work carried out in the above investigations. The results are presented briefly in Chapter 5 while Chapter 6 summarises the appended papers which describe the work in more detail.
2 BACKGROUND

2.1 Ceramic Materials

Conventional ceramic materials have been used for a long time in human history because of their refractory properties and the readiness with which they can be produced out of abundant raw materials, such as clays and minerals, containing aluminium, silicon, boron, carbon, nitrogen and oxygen. Typical ceramic materials are metallic oxides, borides, carbides, nitrides or mixtures or compounds of such materials. The earliest applications were pottery and bricks. In the 20th century ceramic materials began to be exploited as functional materials, making use of properties such as resistance to thermal, chemical and mechanical attack as well as thermal and electric insulation. Their inherent hardness and wear resistance have led to their use in cutting tools and ball bearings.

Glass is usually included in the family of ceramic materials and is still a popular container material for food and beverages, due to its chemical stability, gas tightness and ease of manufacture, as well as its low price. It is also important as a fibre reinforcement in polymer matrix composites. A classification of ceramic materials is outlined in Figure 2.1.

![Classification of Ceramic Materials](image)

**Fig. 2.1.** A common definition of the family of ceramics.

The beneficial properties of ceramics mentioned above and including high elastic modulus, high melting point and relatively low thermal expansion are the result of strong covalent and/or ionic bonding. Unfortunately, such bonding, often in combination with complex crystal structure leads to a resistance to dislocation processes and therefore a resistance to plasticity. Consequently, ceramics are brittle which causes them to fail in a catastrophic manner and, in the case of a specific specimen, at an unpredictable load. The strong bonding forces also lead to a high theoretical strength, which can be defined as the force per unit area needed to separate two atom planes, estimated as:
where $E$ is Young's modulus, $\gamma$ the specific surface energy (which is a measure of bonding strength) and $a_0$ is the interatomic spacing. For example the estimated theoretical strength of silicon nitride is as high as 10 GPa. However, in practice only 500–1000 MPa is achieved in most ceramics. The underlying reason for this is that when ceramics are loaded mechanically, the bonding permits very little plastic deformation, a high level of stress intensification exists at defects. Thus at a sufficiently large defect, the theoretical strength can be exceeded locally even though the nominal stress on the material is relatively low. All materials contain populations of defects more or less randomly distributed with respect to their position and size. As a consequence, ceramics exhibit a statistical range of strengths from specimen to specimen of one and the same material. A second consequence is that they exhibit an influence of size on the average strength such that a small specimen will have a higher strength on average than a larger specimen. These statistical effects can be described in terms of statistical treatments, for example that proposed by Weibull and described in section 4.6.

A relation between fracture of a material and the flaw size gives a more realistic value of the strength than the theoretical one. Griffith suggested for fracture in a brittle material by propagation of an existing internal crack the following relationship:

$$\sigma_c = \sqrt{\frac{2E\Gamma}{\pi c}}$$

where $\sigma_c$ is the fracture strength, $\Gamma$ is the fracture surface energy, $E$ is Young's modulus and $c$ is the crack length. Similar relationships have subsequently been developed within the framework of linear elastic fracture mechanics.

The strength of ceramics does not improve significantly at elevated temperature even though creep processes may relax the stress intensification effect to some extent. This is because ceramics are susceptible to time-dependent, stable crack growth at high temperatures.

### 2.2 Composites

Composites are materials consisting of two or more constituent phases. The geometrical arrangement of the constituents which has an important influence on properties can in principle be chosen arbitrarily. The present discussion is restricted to composites in which one constituent exists in the form of particles or fibres.

Maybe the first examples of ceramic composites are from ancient Egypt, where bricks have been found reinforced with straw. Nature itself provides us with many examples of successful composites; for example wood and bone are fibre reinforced composites. The reason for reinforcing ceramics with for example fibres or particles is to improve the mechanical properties, above all toughness, but also wear resistance and creep strength. It follows from the discussion in section 2.1 that decreasing the size and number of defects in a material will increase the strength and developments in ceramic production have led to significant improvements in this respect. However, it is very difficult to achieve a totally flaw-free ceramic. Reinforcing with another phase is a way to render the material less flaw sensitive, i.e. to be able to survive higher loads with the same defects in the material. Microstructural mechanisms that hinder the crack development in the material or that dissipate the fracture energy in other ways than propagating the crack are described in section 2.2.1. Already here it
can be noted that the toughening and stress-strain behaviour achieved with long fibre reinforcement is distinctly different from that achieved in short fibre and particle reinforcement. In the former, fracture occurs by a gradual evolution of microstructural damage and thus the undesirable brittle fracture normally observed in ceramics is avoided. Long-fibre reinforced ceramics are produced in a variety of morphologies both conventional laminates and various woven architectures. Unfortunately, they are not as easily produced as particulate and short fibre composites, which can be prepared by powder techniques. Several methods of preparation have been described as described in section 2.2.5.

In aerospace applications ceramic matrix composites are attracting increasing interest. These composites could work at temperatures much above those for currently used superalloys. It is also favourable to replace the high temperature alloys with a lighter material. The use of ceramic composites in the hot parts of a jet engine will reduce the need for cooling air, leading to higher thrust-to-weight ratio and reduced specific fuel consumption. The hazardous exhaust emissions from the combustion will also decrease.

There are two main groups of materials used as matrices in CMC’s (ceramic matrix composites) namely, non-oxides (e.g. SiC, Si₃N₄) and oxides (e.g. Al₂O₃, ZrO₂, Y₃Al₅O₁₂ (YAG), Al₃SiO₁₃ (mullite)). These monolithic ceramics can be reinforced with a second phase giving the composite different properties than those of the constituents separately. This second reinforcing phase is usually incorporated in the form of particles, fibres or platelets (see Figure 2.2). Particles are most commonly used in the form of carbides (SiC, TiC) and oxides (Al₂O₃, ZrO₂). Also used are nitrides (TiN and Si₃N₄) and TiB₂. Fibres can be long or short or in the form of whiskers, which are short single crystal fibres. SiC, TiB₂ and Al₂O₃ are available in whisker form. Short fibres are often Al₂O₃ or Al₂O₃/SiO₂ combinations. Some commercially available long fibres are listed in Table 2.1.

![Fig. 2.2. Schematic illustration of principle composite microstructures. (Courtesy R. Warren).](image)

A way to eliminate chemical reaction between fibre and matrix, and minimise thermal expansion mismatch (which can lead to cracking) is to use the same material in the matrix and the fibre (for example single crystal aluminium oxide fibres in an aluminium oxide matrix). Such a composite can exhibit better properties than a bulk polycrystalline form of the same material partly because fibres generally have superior properties and partly because the presence of fibres introduces a system of continuous parallel interfaces into the material which in effect act as a second phase. Indeed, a second phase, a so-called interphase, is often introduced at the interface, e.g. by fibre coating before consolidation. More details about interfaces are given in section 2.2.2.
Table 2.1. Commercially available long fibres for composite reinforcement. (Various sources.)

<table>
<thead>
<tr>
<th>Non-oxide fibres</th>
<th>Composition</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicalon</td>
<td>Si, C, O</td>
<td>Nippon Carbon Co.</td>
</tr>
<tr>
<td>SCS</td>
<td>SiC with W or C core</td>
<td>Textron Spec. Materials</td>
</tr>
<tr>
<td>Tyranno</td>
<td>Si,C + Ti or Zr</td>
<td>Ube Ind.</td>
</tr>
<tr>
<td>B</td>
<td>B with W or C core</td>
<td>Textron Spec. Materials</td>
</tr>
<tr>
<td>Oxide fibres</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FP</td>
<td>Al,O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DuPont</td>
</tr>
<tr>
<td>PRD-166</td>
<td>80 Al,O&lt;sub&gt;3&lt;/sub&gt;/20 ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DuPont</td>
</tr>
<tr>
<td>Altext</td>
<td>85 Al,O&lt;sub&gt;3&lt;/sub&gt;/15 SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Sumitomo</td>
</tr>
<tr>
<td>Saffil</td>
<td>95 Al,O&lt;sub&gt;3&lt;/sub&gt;/5 SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ICI</td>
</tr>
<tr>
<td>Almax</td>
<td>Al,O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Mitsui Mining</td>
</tr>
<tr>
<td>Nextel 312, 440, 480</td>
<td>Al, Si, B, O</td>
<td>3M</td>
</tr>
<tr>
<td>Nextel 550, 720</td>
<td>Si, Al, O</td>
<td>3M</td>
</tr>
<tr>
<td>Nextel 610, 650</td>
<td>Al,O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3M</td>
</tr>
<tr>
<td>Saphikon (Sapphire)</td>
<td>single crystal Al,O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Saphikon Inc.</td>
</tr>
<tr>
<td>Saphikon (YAG-alumina)</td>
<td>single crystal eutectic, Y,Al,O</td>
<td>Saphikon Inc.</td>
</tr>
</tbody>
</table>

It must also be emphasised that composites can have totally different properties and behaviour at low and high temperature, and all data on properties must be accompanied by the temperature at which the data was obtained. As most ceramic matrix composites are intended for high temperature use the behaviour at elevated temperatures is most important. However, high temperature always involves increased difficulties in experimental set up and measurement and in general the reliability of results will therefore be less than for measurements made at room temperature. The properties at lower temperatures are important even for high temperature materials since in general they will also experience excursions at low temperature. Here toughness is of critical significance.

### 2.2.1 Stress-Strain Behaviour of Long Fibre Composites

As mentioned above during loading of brittle materials very high local stresses arise around defects in the material, which means that the strength of the material to a large extent depends on the size and frequency of defects. Processing is being constantly improved to minimise flaws but another important way to increase strength of ceramic composites is to reduce the local stress intensification (or increase the energy of fracture) by a number of toughening mechanisms. Continuous fibre reinforcement in ceramics can provide significant toughening by mechanisms described below. Moreover, such reinforcement can also in certain circumstances prevent the brittle catastrophic failure, characteristic of a monolithic ceramic and instead lead to a pseudo-plastic behaviour. Here toughness means damage tolerance, i.e. the capacity of the material to avoid catastrophic failure by redistributing local stresses exceeding the fracture strength, for example at defects in the material. This is not the same as the fracture toughness, which is the critical stress intensity factor as defined in linear fracture mechanics (see eqn. 2.3 below). The following description of the fracture mechanics of a continuous unidirectional fibre composite is also valid for cross-plies if only fibres lying in the loading
direction are considered to contribute to the proposed mechanisms, the other fibres being considered to be part of the matrix.

Of particular importance are firstly the interface bond strength (or rather its fracture resistance) and secondly the interface sliding resistance (friction stress) of the debonded interface. One extreme case is where the fibre and matrix remain fully bonded up to the composite fracture. This leads to a brittle failure, with a typical stress-strain curve being seen in Figure 2.3a). Here linear elastic fracture mechanics (LEFM) can be applied, fracture stress being determined by the fracture toughness of the material and the largest strength-determining defect:

\[ \sigma_F = Y \frac{K_{ic}}{\sqrt{\pi c}} \]  \[2.3\]

where \( K_{ic} \) is the fracture toughness, \( c \) is the defect size and \( Y \) is a dimensionless constant dependent on the sample and stress distribution geometry.

A second type of fracture is also brittle but some limited crack growth occurs before failure, shown by a reduced stiffness (Figure 2.3b)). Examples of processes leading to such subcritical crack growth and a toughening of the composites can be crack deflection, crack bridging, fibre pull-out, microcracking and phase transformation.

The third type of fracture (Fig. 2.3c)) is pseudo-plastic and is observed in unidirectional long-fibre composites with a weak interface between matrix and fibre. The loading must be axial. This type of fracture will be discussed further below. Unidirectional and multidirectional composites will be discussed separately, as their fracture behaviour and appropriate models can differ quite significantly.

---

**Fig. 2.3.** Three types of stress-strain curves observed in ceramic composites.

### 2.2.1.1 Unidirectional Long-Fibre Composites

As mentioned above one extreme case in a composite is where the matrix and fibre are strongly bonded to each other resulting in a brittle fracture. The other extreme is the case where the fibre is fully debonded with an interface friction that vanishes after the first fracture of one of the constituents. In this case the deformation and fracture behaviour can be modelled by the well-known simple rule of mixtures for fracture strength of continuous composites. This model rarely gives an accurate description of stress-strain behaviour because the interfacial friction is seldom low. However, the model is important as a basis for more realistic models.

**Simple Rule of Mixtures Model**

This model is valid for a long fibre CMC if the following 4 assumptions are made, namely i) that the constituents of the composite have the same properties in-situ in the composite as they have individually, and ii) only unidirectional loading is considered and no account is
taken of constraint effects or any stress concentration that may arise locally and iii) the model
assumes that all fibres have the same strength, which of course is not exactly true for a system
with ceramic fibres which exhibit a scatter in strength and finally iv) when the first constituent
creaks (here assumed to be the matrix) it loses all load bearing capacity, i.e. interfacial friction is
not taken into account.

The stresses in a composite with long unidirectional fibres are given by the universal rule
of mixtures:

\[ \sigma_c = \sigma_f V_f + \sigma_m V_m \]  \hspace{1cm} [2.4]

where \( \sigma_c \), \( \sigma_f \) and \( \sigma_m \) are the stresses in the composite, fibre and matrix respectively. \( V_f \) and \( V_m \) are
the volume fractions. In the fibre direction, this system also obeys the iso-strain rule,

\[ \varepsilon_c = \varepsilon_m = \varepsilon_f \]  \hspace{1cm} [2.5]

which indicates that the strains of both constituents are the same and given by the composite
strain. The iso-strain rule is valid until the first crack is created.

The stress-strain curves of the constituents in a ceramic matrix composite can usually be
represented as in Figure 2.4. Both the matrix and fibres behave in a brittle manner, i.e. they
deform elastically until fracture. The fibres are normally of a higher strength and elastic stiffness
than the matrix (an exception is glass-fibres in a ceramic matrix since the fibres may have a
lower elastic modulus). From these stress-strain curves the elastic behaviour of the composite
can be deduced. Hooke’s law and the iso-strain rule gives

\[ \sigma_c = E_f \varepsilon_f = E_f \varepsilon_c \]  \hspace{1cm} [2.6]

\[ \sigma_m = E_m \varepsilon_m = E_m \varepsilon_c \]  \hspace{1cm} [2.7]

Then from the ROM in stress (eqn. 2.4)

\[ E_c \frac{\sigma_c}{\varepsilon_c} = \sigma_f V_f + E_m V_m \]  \hspace{1cm} [2.8]

Fig. 2.4. Stress-strain curve of the fibre and matrix in a typical ceramic matrix composite.
It follows from Figure 2.4 and the iso-strain condition that with increasing load (i.e. increasing strain) the first thing to occur is that the matrix cracks. Then two different situations can arise depending on the volume fraction of reinforcing fibres. If the amount of fibres is below a critical volume fraction the fibres will not be able to carry the extra load transferred to them when the matrix cracks, and they will also break. Then the composite fracture stress is given by the ROM in stress as:

$$\sigma_{cF} = \sigma_{mF} V_m + \sigma_f^* V_f \quad \text{for } V_f \leq V_{crit} \quad [2.9]$$

where $\sigma_f^*$ is the stress on the fibre when it is strained to the matrix fracture strain. However, if $V_f > V_{crit}$, the composite will be able to continue to carry load, all load being transferred to the fibres. Then the composite fracture stress is described by:

$$\sigma_{cF} = \sigma_{FF} V_f + 0 \cdot V_m = \sigma_{FF} V_f \quad \text{for } V_f > V_{crit} \quad [2.10]$$

These two equations are plotted against $V_f$ in Figure 2.5, which therefore predicts the dependence of UTS (ultimate tensile strength) on $V_f$.

![Fig. 2.5. A typical ROM diagram for ceramic matrix composites where axial fracture strength is shown as a function of fibre volume fraction.](image)

A number of cases of behaviour intermediate between the two extremes described above can be identified. An important example is the case of a fully debonded fibre with a significant interfacial friction and a fibre fracture stress and strain significantly greater than that of the matrix. Here the matrix can suffer multiple cracking and still carry a proportion of the composite load while transferring load to the fibres. Each matrix cracking event leads to additional load transfer uniformly distributed over all the fibres. These condition lead to a non-linear, pseudo-plastic stress-strain behaviour and it is this behaviour that is sought in the development of the majority of ceramic composites.

**Pseudo-plasticity and global load-sharing models**

If there is an appropriate amount of fibres and they are sufficiently weakly bonded to the matrix, a continuously reinforced CMC can fracture in a plastic way (Fig. 2.6). This pseudo-plastic behaviour is quite well understood\(^{10,11,12}\) and a quantitative model is outlined here with
Background

reference to the schematic stress-strain curve in Figure 2.6. The model takes account of interfacial friction and the statistical variation in fibre fracture stress.

The first part of the curve is elastic deformation. At point A the first matrix crack is initiated as the matrix reaches its fracture strain. The fibres will remain intact, provided that the bonding between matrix and fibres is weak enough for the crack to deviate at the interface. A well-known model that describes the conditions for the first matrix crack is the so-called ACK-model (Aveston, Cooper, Kelly). It is based on an energy balance, where supplied energy, i.e. the external load plus the strain energy released from the matrix when relaxing, must be larger than or equal to the energy absorbed in creating the crack. The absorbed energy consists of the matrix fracture energy plus strain energy absorbed by the fibres plus energy absorbed by friction when matrix slides back over the fibres.

The ACK model derives the stress and strain in the composite at first matrix crack:

\[
\sigma_c(mF) = \left[6\pi r_m V_m^2 E_c^2 E_f / (1 - V_f) E_m^2 r_f\right]^{1/3}
\]

\[
\varepsilon_c(mF) = \sigma_c(mF) / E_c
\]

where \(\tau\) is the interfacial friction and \(r\) the fibre radius and \(\Gamma\) is the matrix fracture energy. Upon further loading the fibres and matrix continue to strain and the matrix exhibits multiple fracture, i.e. cracks form at regular distances along the matrix created by the release of additional strain energy built up by loading. In order to obtain multiple matrix cracking the strain to failure of the matrix must be less than the fibre strain to failure, and the fibre-matrix bonding must be weak enough to favour debonding instead of fibre breakage. Furthermore, the volume fraction of fibres and the fibre strength must be high enough to carry the total load alone. Marshall, Cox and Evans had a similar approach, but they also treated short cracks in contrast to Aveston, Cooper and Kelly who only analysed long cracks. An extension of the ACK model was made by Budiansky, Hutchinson and Evans where they incorporated thermal residual stresses.

Crack saturation is achieved at point B of the curve in Figure 2.6, where there is no longer enough matrix strain energy to create new cracks. The crack spacing at saturation is characteristic for the system and the load situation. Zok & Spearing have modelled the conditions during multiple cracking concluding that crack saturation occurs at the saturation stress:

\[
\sigma_{\text{esat}} = 1.3\sigma_{c\text{(mF)}}
\]

at an average crack spacing of

\[
l_{\text{esat}} = 2.68x_t
\]

where \(x_t\) is the transfer length, i.e. the distance from the crack at which the maximum matrix stress is reached and given by a simple load balance:

\[
2\pi r x_t = \pi r^2 \sigma_m
\]

giving
where $\sigma_m$ is the matrix stress and $V_m$ and $V_f$ are the volume fractions of matrix and fibre.

$$x_i = \frac{\sigma_m r V_m}{2\tau V_f}$$

[2.16]

Cox et al.\textsuperscript{13} showed that variation in fibre strength had very little effect on the multiple matrix cracking strain.

During increased loading the fibres begin to crack successively as their fracture strength is reached. Although the matrix is fragmented, the fragments can still carry some load, due to interfacial friction between matrix and fibre. The fibres continue to fracture until they reach a critical length, given by the simple shear lag model:

$$L_c = \frac{r\sigma_{f(\text{lim})}}{\tau}$$

[2.17]

where $\tau$ is the interfacial friction stress, $\sigma_{f(\text{lim})}$ is the stress at the centre of the fibre fragment of this length and $r$ is the fibre radius. Point D of the curve shows the ultimate tensile strength of the composite. Between D and E there are continued fibre fracture and pull-out. Even when all fibres are fractured the interfacial friction provides continued load bearing capacity until full fibre pull-out has occurred at point E. This is the basis of Curtin’s model.\textsuperscript{16}

The Curtin model is based on considering partly the friction stress and partly the statistical nature of fibre strength. When a fibre breaks, the stress will increase with distance from the break due to shear lag. (At the actual crack the stress is zero). However, the fibre strength increases with decreasing length due to the dependence of strength on volume. Curtin defined a characteristic fibre length, $\delta_{\text{ch}}$, as the mean length of the fibre fragments when they have attained saturation multiple fracture. $\sigma_{\text{ch}}$ is the average strength of fibres with this characteristic length. $\sigma_{\text{ch}}$ is formally defined as the stress giving a survival probability $P_s = 0.368$. 

Fig. 2.6. Pseudo–plastic fracture behaviour of a long fibre reinforced ceramic matrix composite. (Courtesy R. Warren).
With simple shear-lag conditions (eqn. 2.17) and applying the Weibull equation (eqn. 4.1) expressions for \( \delta_{ch} \) and \( \sigma_{ch} \) as a function of fibre radius, \( r \), Weibull modulus, \( m \), and friction stress, \( \tau \), can be derived.

\[
\delta_{ch} = \left( \frac{r \sigma_0 l_0^{1/m}}{\tau} \right)^{m/m+1} \quad [2.18]
\]

and

\[
\sigma_{ch} = \left( \frac{\tau \sigma_0 L_0}{r} \right)^{1/m+1} \quad [2.19]
\]

where \( \sigma_0 \) and \( L_0 \) are the scale constants in the Weibull equation.

From this is then derived an expression for the ultimate tensile stress (stress maximum of the stress-strain curve) and for the corresponding composite strain at maximum stress:

\[
\sigma_{cu} = V_f \sigma_{ch} \left[ \frac{2}{m+2} \right]^{1/m+1} \left[ \frac{m+1}{m+2} \right] \quad [2.20]
\]

\[
\varepsilon_{cu} = \frac{\sigma_{ch}}{E_f} \left[ \frac{2}{m+2} \right]^{1/m+1} \quad [2.21]
\]

The average pull-out length is given by

\[
L_p = \lambda'(m) \frac{\delta_{ch}}{4} \quad [2.22]
\]

where \( \lambda' \) describes the fibre fragment frequency distribution and lies between 0.9 and 1 for typical \( m \) values.

The work of fracture is given by

\[
W_p = \lambda'''(m)V_f \sigma_{ch} \frac{\delta_{ch}}{12} \quad [2.23]
\]

where \( \lambda''' \) lies between 0.8 and 1.2 for typical values of \( m \) (between 4 and 10). This provides a measure of the toughness of the material.

The above description of the stress-strain behaviour expressed through equations 2.11–2.23 reveals the importance of the fibre fracture stress and its statistical variability as well as the nature of the fibre/matrix interface. To achieve pseudo-ductile behaviour the strain to failure of the majority of the fibres should be significantly higher than that of the matrix and the bonding between the fibres should be sufficiently weak to give full debonding either prior to or during loading. Ideally the interface should remain bonded until matrix fracture since this ensures the most favourable transverse and shear properties. Criteria for debonding in terms of interface and fibre fracture are discussed in section 2.2.2.
The influence of the interfacial friction on the shape of the stress-strain curve is readily revealed through the equations. For example, increasing $\tau$ raises the matrix cracking stress levels, raises the UTS but reduces the total strain to failure and work of fracture. Similarly increasing the Weibull modulus, $m$, increases the tensile strength and decreases the failure strain. It is also interesting to note that decreasing fibre radius reduces the matrix cracking stress but has a favourable effect on UTS and work of fracture.

Optimum interface characteristics can rarely be achieved in a simple, two-component fibre/matrix combination. Instead, some form of interfacial layer between fibre and matrix has to be applied (see section 2.2.2).

If fibre-matrix debonding occurs only partially and in association with matrix cracking, then fracture of the composites can occur by passage of a single crack with a limited process zone of bridging and fracturing fibres. Such behaviour provides an intermediate toughening that can be modelled in terms of a modified fracture mechanics.

**Process zone toughening mechanisms**

As indicated earlier the passage of a matrix crack can lead to a partial debonding of the interface. In general, the debonded length and consequently the maximum stress on the fibre in the crack plane will increase with distance behind the crack tip. Thus fibre fracture will occur at some distance behind the crack tip leaving a zone of unbroken fibres just behind the tip and moving with it. This zone of bridging fibres can lead to an increase in toughness (relative to the unreinforced matrix toughness) in a number of ways. The zone develops during the initial stages of crack growth and eventually attains a steady state size. Thus initially an increasing crack resistance, so-called R-curve behaviour, is observed, where $R$ stands for resistance to fracture (units of energy). This is in contrast to the case of an ideally brittle material, where the fracture toughness is independent of the crack extension. In Figure 2.7 the different behaviour is shown. For the experimental determination of crack resistance curves, a crack of a known length is introduced in the specimen, and together with applied load it is possible to calculate apparent fracture toughness.

![Fig. 2.7. Materials with a flat and a rising crack-resistance curve (R-curve).](image)

**Fibre bridging**

Crack bridging in fibre reinforced composites is vital for the enhancement of the composite fracture resistance. Crack bridging is dependent on the properties of the fibre-matrix interface. The interface bonding must be relatively weak for debonding of the interface to occur, with following frictional sliding upon crack extension.
Two alternative models are used to describe the bridging zone. The first is called the stress intensity approach, where one regards a closure stress on the crack, trying to close it. $K$, is integrated along the bridging zone. The second model is an energy approach, where the strain energy release rate, $\Delta G$, is considered. Both models should give the same result and they both require knowledge of the fibre stress as a function of the distance behind the crack tip or the crack opening which depends on the interfacial bonding. The two models are related through the expression

$$G_{lc} = K_{lc}^2 \frac{(1 - \nu^2)}{E} = \Gamma,$$  \hspace{1cm} [2.24]

for plane strain, mode I fracture. $G_{lc}$ is the critical strain energy release rate necessary to overcome the fracture surface energy $\Gamma$.

Marshall, Cox and Evans\textsuperscript{13} investigated how fibre bridging affects the stress intensity at the crack tip. They showed that the stress intensity at the matrix crack tip can be decreased by a significant amount by fibres bridging the zone. When steady state is reached, the crack growth energy is independent of crack size.

**Fibre fracture and pull-out**

In the bridging zone most of the applied load is carried by the fibres. The stress in a single fibre is highest just at the matrix crack, and decreases further away from the crack. If the fibre strength were uniform all along the length, the fibre would fail at the matrix crack. But as fibre strength varies along the length, due to statistical distribution of flaws, fibre failure can also take place away from the matrix crack. Then the fibre is pulled out from the matrix during final failure, and the energy will dissipate through frictional sliding between the matrix and the fibre. Thouless and Evans\textsuperscript{19} analysed a fibre pull-out mechanism for fibres with a Weibull distributed strength. The result was that the shape of the load-displacement curve depends on the width of the fibre strength distribution. Cao and Thouless\textsuperscript{20} show similar results.

**Creep**

Creep is defined as time-dependent deformation. When the creep behaviours of the constituents are known and assuming a condition of iso-strain rate it is quite straightforward to predict the creep of a continuous fibre composite. The ROM in stress can in this case be applied for steady-state creep, i.e. when the creep rate is constant in both fibre and matrix. For non-linear creep in which the strain rate of the constituents is transient a numerical model must be used. For steady state creep:\textsuperscript{21}

$$\epsilon_c = \epsilon_f = \epsilon_m \hspace{1cm} \text{(iso-strain rate)}$$  \hspace{1cm} [2.25]

$$\epsilon_f = A_f \exp\left(-\frac{Q_f}{RT}\right) \sigma^n,$$  \hspace{1cm} [2.26]

$$\epsilon_m = A_m \exp\left(-\frac{Q_m}{RT}\right) \sigma^n,$$  \hspace{1cm} [2.27]

where $A_f$, $A_m$, $n_f$ and $n_m$ are constants. $Q$ is the activation energy, $R$ the gas constant and $T$ absolute temperature. Figure 2.8 illustrates how for a given composite strain rate the stresses in
Background

the fibre and matrix are fixed by the iso-strain rate condition while the composite stress is related to the stresses and volume fractions of the constituents by the ROM in stress.

![Graph showing creep rate versus stress for a CMC obeying iso-strain rate rule.](image)

**Fig. 2.8.** Creep rate versus stresss for a CMC obeying iso-strain rate rule.

In general it is not possible to derive a simple analytical expression from equations 2.25-2.27 for the creep rate of the composite as a function of stress. However, the stress appropriate to a given creep rate can readily be derived by application of the ROM in stress as indicated above. It is then possible to plot creep rate as a function of applied stress on, for example, a log-log scale (Figure 2.9). This plot will generally approximate a straight line thus permitting limited extrapolation as well as determination of an empirical stress exponent $n_c$ for the composite.

![Graph showing log-log scale for composite creep.](image)

**Fig. 2.9.** A log-log scale makes it possible to plot the composite creep conveniently.

For a full description of creep, consideration must also be given to off-axis creep and to fracture processes. Models for these aspects are still not fully developed. Several damage processes such as matrix cracking, fibre fracture, interfacial debonding and interfacial sliding need to be modelled if the damage is to be taken into account. In off-axis loading the more rigid fibres will constrain the creep in the less creep-resistant matrix but the constituents can be assumed to experience a component of pure shear which will dominate the creep behaviour.²²

### 2.2.1.2 Multidirectional Composites

General loading of a 2-D CMC involves both tension and shear loading. The complex load situation makes it difficult to apply the classical models for the mechanical behaviour. If the behaviour of a 2-D material is dominated by the $0^\circ$ plies it is possible to compare it with a 1-D (unidirectional) CMC, taking into consideration only the fibre volume in the $0^\circ$ plies.
Then the models above are valid. A prerequisite for treating a woven composite in the same manner is that the curvatures introduces by weaving have minimal effect on the stress strain behaviour. Some empirical models have been developed to investigate the notched behaviour and they will be discussed in section 2.2.4. A continuum model of damage in ceramic matrix composites, which predicts the stress-strain behaviour during matrix cracking has been developed by Talreja and is applied to a SiC (Nicalon)/CAS composite in reference 25.

2.2.2 Interfaces and Interphases

The fracture behaviour of a ceramic matrix composite is largely ruled by the properties of the fibre/matrix interface. A weak fibre/matrix interface is often a prerequisite for a pseudo-ductile behaviour of the composite (an important exception being CMCs with a porous matrix, as described in section 2.2.3). The bonding must be weak enough for the crack to deviate when approaching the fibre, but still strong enough for successful stress transfer from the matrix to the fibre. Of particular importance are firstly the interface bond strength (or rather its fracture resistance) and secondly the interface sliding resistance (friction stress) of the debonded interface. The interface must be compatible with both the matrix and the fibre to prevent chemical reactions which might lead to an increased bonding and a decrease in toughness. The interface also needs to be refractory to the same extent as the other constituents. To encourage debonding the interphase material can be chosen to have an intrinsically low fracture resistance. Fugitive interphases have been used to create a gap between the fibre and the matrix, the natural topography of the fibre providing the necessary sliding resistance.

In order to achieve the necessary interface debonding certain criteria can be defined. Evans, He and Hutchinson have proposed a model to decide whether a crack in the composite will lead to debonding of the fibre or pass through the fibre. The criteria for crack deflection depends on the relative fracture energies of the fibre and the interface, on the relative elastic constants of fibre and matrix and on the angle between the crack plane and the interface. The influence of these parameters are summarised in Figure 2.10. In most ceramic composites, having similar elastic properties of matrix and fibre, it is found that the fracture energy of the interface should be less than 25% of the fibre fracture energy for debonding to occur.

![Fig. 2.10. Criteria for crack deflection at a plane interface.](image)

The importance of the bonding and friction between the fibre and the interface for the performance of the composite is well established. It is therefore of great interest to be able to measure them experimentally. There are number of different ways in which this can be done.
The most common way to test the interfacial properties is to perform a so-called push-out test or variants of this such as pull-out and push-down tests. In these tests polished sections are made perpendicular to the fibres in actual composites and individual fibres are then loaded using microindentors. In the push-out tests the samples are thin slices around 1 mm thick. The fibre displacement is measured as a function of increasing indentation load to produce stress-displacement curves. A typical push-out curve is shown in Figure 2.11. From the curve can be deduced the elastic bonding of the fibre (the first part of the curve), the stress needed for debonding of the fibre and the friction coefficient between the matrix and the fibre. Often the sample is reversed and the fibre is pushed back again, giving the friction alone since there is no longer any bonding.

![Figure 2.11](image)

**Fig. 2.11.** Typical load deflection curve for fibre push-out exhibiting progressive debonding followed by push-out. $P_i$, $P_d$ and $P_f$ are defined as the load at the initiation of debonding, the debonding load and the friction load respectively. The undulating frictional resistance is attributed to varying fibre diameter. (Courtesy D. Le Pagne).

It is of course interesting to investigate the behaviour in tension, which will be the mode of stress experienced by the fibre during normal loading, parallel to the fibre direction. For this reason a pull-out test is sometimes performed. This test is more difficult to perform as a special composite must be produced, with the fibre sticking out from the matrix in order to be gripped. It is not easy to produce such a composite and it is also difficult to clamp the fibre without breaking it. This test is often used for glass fibres in epoxy or other polymer matrix composites.

Fragmentation tests are also a common way to measure the interfacial strength between a fibre and the surrounding matrix. Most commonly they are applied to polymer and metal matrix systems in which case it is the fibre that fragments. However, the same principle could be applied to a CMC by observation of matrix fragmentation. Typically, a fibre is embedded in a polymer matrix and a tensile load is applied to the specimen. With increasing load, the fibre fractures in fragments of shorter and shorter lengths, until saturation is reached. The interfacial shear stress can be estimated form the fragment length distribution. The length of the fragments are measured by visual inspection which means that this test could only be applied to transparent matrices or after leaching away the matrix.

The use of hysteresis measurements made on a composite at stresses above the matrix cracking stress but below the saturation stress is a methodology that could provide information of the behaviour of real composites. It has advantages over the push-in and push-through tests.
as this method gives information about the average behaviour of the actual composite, not only a single fibre. In such a test the stiffness loss, the interfacial resistance of sliding and debonding as well as the residual stress could be related to the unload/reload hysteresis and permanent strain. A description of this test method is given in reference 31 and the same authors have experimental results from tests on SiC/CAS and SiC/SiC unidirectional composites.  

2.2.3 Porous Matrix Composites

An alternative to the use of a weak interphase to enhance crack deflection is the concept of porous matrices, where the matrix itself acts as a crack deflection path. Delamination has been shown to occur in the matrix and the crack deflects into a plane parallel to the loading direction. A porous matrix acting in this way allows matrix and fibres to be bonded together and still achieve the damage tolerance of conventional CMCs. The concept has been shown to work successfully, but the challenge is to obtain porosity that is uniformly distributed and which remains stable during thermal exposure. A recent concept for achieving a stable, uniformly distributed porosity is by introducing smaller particles of another material in a continuous network of matrix particles. Another method to bond the matrix particles together to strengthen the matrix without shrinkage is to use cyclic impregnation and pyrolysis of a solution precursor.

An advantage of porous matrix composites is that avoiding the extra step of fibre coating makes the processing of the composite cheaper and simpler. A coating step also introduces difficulties in reproducibility since the interface is difficult to apply and retain over the entire surface of a complex fabric.

The processing method used in reference 33 was pressure filtration for packing the powder followed by cyclic infiltration and pyrolysis of a liquid precursor and giving a particle bonding without shrinkage. Recently a simpler and less time consuming fabrication method has been developed by Haslam et al. After infiltration of the fibres with sub-micron ceramic particles the powder is treated to produce a special interparticle pair potential which allows the powder compact (previously consolidated by pressure filtration) to be fluidised. A treatment with HCl produces a strong matrix without shrinkage via an evaporation/condensation sintering mechanism.

The main difficulties with the porous matrix concept are i) it is difficult to balance fibre dominated properties like longitudinal tensile strength with matrix dominated properties such as compression or trans-thickness tensile strength, ii) at sufficiently high temperature the matrix will begin to densify by sintering leading to a loss of the crack-deflection mechanism and often a coarsening of porosity and iii) the microporosity is interconnected; thus the composite is not hermetically sealed, and allows rapid ingress of the environment.

Because the strength of a porous matrix is generally less than that of dense matrices, the interlaminar shear strength is lower, about 15 MPa compared to about 30 MPa for dense matrix composites with comparable constituents.

In a porous matrix a crack can exist without the extremely high stress concentration usually associated with cracks in a continuum. Therefore, fibre fracture within a very porous matrix must initiate within the fibre itself, e.g. from flaws on the surface or inside the fibre. This means that the fibres fracture in a similar manner to when they exist in a dry bundle or in a woven cloth without matrix.

The creep of a porous matrix CMC has been investigated by Levi et al. The creep rates were lower than the values expected for the fibres alone, which indicates that the matrix was able to sustain some of the creep load.

The bend strength of a Nextel 720/porous zirconia-mullite composite was more than 160 MPa for the 0/90 fibre orientation and >80 MPa for the ±45° fibre orientation. The composite showed a moderate notch-sensitivity and R-curve behaviour. The same bend
strength (160 MPa) was found for a 0/90 Nextel 720/mullite composite.\(^8\) The composite exhibited pseudo-plastic and damage tolerant fracture behaviour. Long term heat-treatment at 1250°C (400 hrs) and short-term at 1500°C (3 hrs) had little effect on the damage tolerant behaviour and strength. A unidirectional Nextel 720/mullite composite exhibited damage-tolerance and a strength of about 280 MPa, which were retained also after short-term heat-treatment at 1500°C.\(^9\) However, after 2 hrs at 1600°C the material became brittle, due to degradation of the fibre. The outer layer of the fibre consisted only of silica, the alumina was depleted and reacted with the free-silica in the glass phase of the matrix.

### 2.2.4 Notch Sensitivity

For an infinite plate containing an elliptical hole (see Figure 2.12), Inglis\(^4\) was able to show that a uniaxial applied stress \(\sigma\), was magnified at the ends of the major axis of the ellipse so that

\[
\sigma_{\text{max}} = \sigma_u \left( 1 + 2 \frac{a}{\rho} \right)
\]

where \(\rho\) is the radius of curvature of the hole. The term \(1 + 2 \frac{a}{\rho}\) is defined as the stress-concentration factor \(k\), and is a basic term in linear elastic fracture mechanics (LEFM). It can be seen from equation 2.28 that \(k\) increases with increasing crack length and decreasing crack radius. The influence of hole diameter to plate width ratio on the stress-concentration factor for axial loading of a bar with a transverse circular hole is shown in Figure 2.13.

\[\text{Fig. 2.12. Elliptical hole in infinitely large panel.}\]

\[\text{Fig. 2.13. Stress intensity factor as a function of hole to width ratio for a bar with a transverse hole.}\]

A metal or another ductile material can plasticise around the notch-tip to decrease the stress-concentration factor before the stress-levels reach the intrinsic strength of the material which gives it a notch-insensitive behaviour. A brittle material, on the other hand, is fully notch-sensitive, i.e. the stress cannot be redistributed around the notch tip in order to decrease the stress-concentrations. A ceramic matrix composite can exhibit reduced notch-sensitivity through a number of mechanisms that redistribute stress concentrations including multiple
matrix cracking, fibre pull-out after fibre breakage and fibre bridging. In a fully notch-insensitive material the only reduction in strength is that due to the reduced cross-section area.

Brittle-matrix composites are considered to be divided into three main classes\textsuperscript{41} (see Figure 2.14) each associated with different mechanisms of stress redistribution. Class I behaviour is dominated by fibre bridging and pull-out from a single crack. It is the pull-out tractions that redistribute the stresses. However, the interfaces are “strong” which leads to notch-sensitive tensile properties. The behaviour can be treated by large scale bridging mechanics (LSBM) based on bridging and pull-out.\textsuperscript{42}

In class II materials the fibres do not fracture initially. Instead multiple tensile matrix cracking occurs which leads to the stress redistribution. Class II materials are often referred to as “matrix dominated”. The matrix cracking leads to significant inelastic strain prior to failure but relatively high notch-sensitivity.

Class III materials redistribute stress by shear band formation in the matrix. Their failure is “fibre dominated”, i.e. dominated by stochastic fibre failure giving relatively little inelastic strain in tension. Class II and III material can be distinguished by the ratio of matrix shear modulus to the fibre tensile modulus. When this ratio is small class III behaviour dominates and vice versa.\textsuperscript{42}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.14}
\caption{Three classes of fracture behaviour in CMCs.}
\end{figure}

Stress redistribution as a result of matrix cracking emanating from the notch has been treated in terms of continuum damage mechanics by Genin and Hutchinson.\textsuperscript{43}

Below some different approaches for treating notch-sensitivity in practice will be discussed.

**Inherent flaw model**

A simplified approach to predict the notched strength of laminated composites that utilises concepts of LEFM was proposed by Waddoups et al.\textsuperscript{44} The basis of the model is that the fracture stress, $\sigma_f$, of centre hole notched infinite plate is determined by the equation:

$$K_c = \sigma_f \sqrt{\pi \left( \frac{a}{2} + c_0 \right)} \quad [2.29]$$
where $a$ is the hole diameter, $K$ is a critical stress intensity factor and $c_0$ is the length of two cracks on opposite sides of and adjacent to the hole (see Figure 2.15). In fibre composites it is assumed that the damage zones adjacent to the holes are equivalent to the cracks. It is also assumed that both $K$ and $c_0$ are constants, that is independent of hole size, for a given material. The two parameters cannot readily be related to actual physical processes in the material but provided that they are found experimentally to indeed be constants then they offer a convenient means of comparing materials as well as providing a means of strength prediction via equation 2.29. Thus the embrittlement of a composite can be expected to lead to a reduction of both $K$ and $c_0$.

In order to apply eqn 2.29 to experimentally determined strength values, these must first be corrected for the finite width effect by applying the factor $K/3$, where $K$ is the stress intensity factor for a hole in a plate with finite width given by:

$$K = 3.00 - 3.13 \cdot \left( \frac{a}{w} \right) + 3.66 \cdot \left( \frac{a}{w} \right)^2 - 1.53 \cdot \left( \frac{a}{w} \right)^3$$

[2.30]

The corrected stress value is in effect the predicted strength of an infinite plate.

Fig. 2.15. Fracture mechanics model for circular hole, used by Waddoups et al. (From 46).

Point stress criterion

Whitney and Nuismer suggest an alternative to the Waddoups model based on the stress distribution adjacent to the notch. The stress decreases from the maximum value with distance from the notch. Fracture is assumed to occur when the stress at a point, located at a characteristic distance $d^{\text{PSC}}$ from the notch edge reaches the unnotched strength of the material, $\sigma_c$. The term $d^{\text{PSC}}$ is the distance over which the material must be critically stressed in order to find a sufficient flaw size to initiate failure. The assumption that $d^{\text{PSC}}$ is a material property independent of laminate geometry and stress distribution is not valid.

Kim et al. suggest a modified PSC, where $d^{\text{PSC}} = k^{-1}(2R/W)^m$, where $k$ is the notch sensitivity factor corresponding to $2R$ (notch diameter) and $W$ (width), and $m$ is an exponential parameter. The modified PSC is as follows:
\[
\frac{\sigma_N^w}{\sigma_0} = \frac{2}{[2 + A_2^w + 3A_3^w - (K_T^w - 3)(5A_6^w - 7A_7^w)]}
\]  

[2.31]

where \( A_2^w = 1/(1+2^{n-1}W^a R^m k^0) \).

This is a 3-parameter model (unnotched strength \( (\sigma_0), k, m \)). These parameters can be determined experimentally by testing one unnotched specimen and two notched specimens with circular holes.

Karlak\(^9\) proposed a modification of the PSC in which the characteristic length \( d_0 \) is a function of the hole radius, \( d_0 = k_0 R^{1/2} \). Pipes et al.\(^{50}\) further extended PSC, introduced a 3-parameter strength model, \( d_0 = k'/(R/R_0)^m \), where \( k' > 0 \) is the notch sensitivity factor and \( 0 < m < 1 \) is an exponential parameter. \( R_0 \) is a reference radius. Problems arise because \( k' \) depends on the selection of \( R_0 \), and small notches may give a negative \( m \).

**Average stress criterion**

Whitney and Nuismer also proposed an average stress criterion. Failure is considered to occur when the average stress over the characteristic distance \( d^{ASC} \) reaches the unnotched strength,

\[
\frac{1}{d^{ASC}} \int_{R}^{R+d^{ASC}} \sigma_0(x,0) dx = \sigma_0
\]

[2.32]

**J-integral approach**

The use of the J-integral is another way of characterising failure. \( J \) is defined as follows

\[
J = \int_C (W dy - T \cdot \delta u / \delta x) ds
\]

[2.33]

where \( ds \) is an increment along contour \( C \), \( T \) is a stress vector acting on the contour, \( u \) a displacement vector and \( W \) is the strain energy density, equal to \( |\sigma| d e \). Failure (crack initiation) occurs when \( J \) reaches some critical value, \( J_{IC} \). For either linear or nonlinear elastic conditions, \( J \) is the energy made available at the crack tip per unit crack extension, \( da \). That is, \( J \) is equivalent to the crack driving force.

\[
J = \frac{K^2}{E'}
\]

[2.34]

where \( E' = E \) for plane stress and \( E' = E/(1-\nu) \) for plane strain.

\( J_{IC} \) is an engineering estimate of fracture toughness near the onset of stable crack extension. Shen et al.\(^{31}\) claims that the J-integral approach is a more relevant way to predict failure in structures containing large notches or cracks than strength tests on specimen that are relatively narrow and containing short notches. The results from the latter tests may not be applicable on larger structures.
Bridging laws

Experiments are performed to determine a material’s notch-tip deformation behaviour explicitly, i.e. to determine a bridging law. The opening of a crack bridged by fibres involves stretching of fibres between the surfaces of the crack. The form of the bridging law (the relation between the stress in the fibres and an average local crack opening displacement) depends on the details of the bridging mechanism and properties such as fibre/matrix debonding and frictional sliding as well as elastic stretching of the fibre. From this the notched strength can be derived for different geometries and loading situations. A solution to an integral equation to calculate the crack opening displacements is necessary in order to specify the distribution of closure tractions over the crack surface. The method has physical validity but it is both an experimentally difficult and an expensive method.

2.2.5 Preparation of Ceramic Matrix Composites

In all production of ceramic matrix composites it is important to achieve as dense a product as possible with a minimum of defects. An exception to this are the so-called porous matrix composites (see section 2.2.3 above). Another important demand is to keep the geometry of the composite as desired. This section concerns the preparation of long-fibre composites. Several special techniques are described that have had to be developed because the fibre configuration places large demands on the processing and means that processes developed for monolithic ceramics cannot be used. Necessary processing steps include fibre preforming, fibre coating (before or after preforming), matrix infiltration and consolidation.

Fibre Preforming

A long fibre with small diameter is flexible enough to be woven. This method is used to make large preforms in two or three dimensions, which gives a degree of isotropy. The drawback with a woven preform is that it is hardly possible to avoid local fibre-free areas, especially next to cross-over points, thus creating weak spots. The overall volume fraction achievable is not more than around 40%,\(^{32}\) which is less than for a totally aligned composite. The two most common woven configurations are shown in Figure 2.16, namely plain and satin weave. Plain weave is stiffer exhibiting less slipping than satin weave, but has a higher amount of porosity. On the other hand a satin weave is more flexible and can be stacked in more complex shapes.

![Plain weave and satin weave](image)

Composites may also be reinforced in a so-called cross-ply design. Alternate unidirectional fibre layers are stacked at various angles to each other (e.g. 0/90). The cross-ply laminates have orthotropic properties, (i.e. two-dimensional) and therefore lower tensile strength than a unidirectional composite (loaded in the fibre direction).
**Fibre Coating**

As has been pointed out earlier it is extremely important to optimise the interfacial layer (sometimes referred to as the interphase) in a CMC in order to achieve desired fracture behaviour. Moreover the optimised interphase must be preserved during processing, i.e. no chemical reaction with the matrix or the fibre should occur. The interphase must have either a low intrinsic fracture energy or create an interface that is weakly bonded to either the matrix or the fibre. Another concept is the use of compounds that have some crystallographic planes of easy cleavage and oriented in such a way that they encourage the crack to deflect away from the fibre, for example micas, or mixed aluminates. Certain other oxides and refractory metals have also been identified as promising interphases (see section 3.3.1). Carbon and boron nitride are mechanically suitable interface materials, the drawback being their sensitivity to oxidation in oxidising atmospheres.

So-called fugitive interfaces have recently attracted some interest. In this case, an interfacial layer is applied which is burnt off during presintering, leaving a gap between fibre and matrix. The friction during fibre pullout, needed to dissipate fracture energy to avoid catastrophic failure is assured by the natural roughness of the surfaces of the fibres and the matrix. It is important that the fibre and matrix do not react with each other, leading to bridging of the gap and consequently to a more brittle behaviour. It has been found that variations in fibre diameter could make reproducibility difficult, especially for large fibre diameters.

Interphases are generally introduced by coating the fibre prior to matrix infiltration. Such a coating can be applied with different methods. Chemical vapour deposition (CVD) is a common method which gives even layers permitting accurate control of layer thickness. It is however a rather slow method. The fibre is heated in a vacuum chamber and a gas or gas mixture is passed over the fibre. The gas mixture is chosen so that it will react or decompose when it comes in contact with the fibre, heated to a specific temperature, typically around 1000°C. The resultant coating is fine grained and of high purity and hardness. One possible drawback is that the grains are often columnar, oriented perpendicular to the surface.

Another method is dip coating where the fibre is dipped into a slurry or a sol of the desired interphase material. It is necessary to carry out a binder burn-out and presintering before producing the composite.

Sol-gel coating can also be used to apply a thin coating on the fibre. A slightly different method is hydrothermal deposition, which has been used to give a homogeneous coating of zirconia on an alumina substrate. The advantage with this method is low synthesis temperature, only 100-200°C, and a simple set-up.

Physical vapour deposition, PVD, is another way of coating a fibre. Several different methods can be classed as physical vapour deposition, for example vacuum vapour deposition and radio-frequency (R.F) sputtering. PVD requires lower temperature than CVD which leads to less thermal strain and less formation of defects due to diffusion between the layer and the substrate. R.F. magnetron PVD was used by reference to obtain an interphase on single-crystal alumina (Saphikon) fibres. A small area target was used of the required oxide. The sputtering, assisted by a low-pressure gas, induced a stoichiometric transfer of the oxide from the target onto the fibres. Rotating filament holders assured a uniform coating thickness. The resulting microstructure of the PVD coated layer was columnar, and the scale of the columnar crystal structure could be varied by adjusting the operating conditions (power level and substrate bias for example). Porosity and degree of crystallinity were also affected by the operating conditions.

**Matrix Infiltration Methods**

To produce the final composite, the preform must be infiltrated with the matrix. Ideally, the infiltration should yield the matrix in its final and consolidated form. However, some
methods require a subsequent consolidation process (e.g. slurry infiltration) or a chemical conversion (e.g. pyrolysis of a polymer infiltrant).

Chemical vapour infiltration (CVI) is a method that can yield a matrix without the need of a subsequent step. It has proven capable of giving evenly infiltrated preforms. The matrix is formed in situ by a reaction from a gas mixture that passes through the preform. Normally, a temperature of about 1000°C is used. There are gas mixtures available for almost any ceramic component. C/ SiC and SiC/SiC composites are commonly produced by the CVI route. The gas temperature and pressure play important roles in achieving a successful infiltration with a minimum of residual porosity. In producing large components, premature densification of the surface may necessitate intermediate surface machining operations.

Liquid polymers can be used to infiltrate preforms to give matrices of SiC or Si₃N₄ after pyrolysis. Polycarbosilanes and polysilazanes respectively are used for example in molten form or in solution. They are pyrolysed at a moderate temperature, normally not exceeding 1000°C. During pyrolysis the polymer is transformed into the ceramic. This demands a rather long processing time, since several infiltration/pyrolysis cycles might be necessary to reach a high density. The polymer precursors are also expensive. Carbon/carbon composites are normally produced in this way. Resin transfer moulding (RTM) is a method that already exists within the aerospace industry for polymer matrix composites, and it has been shown to be a useful method also for ceramic matrix composites. The shrinkage can be minimised by incorporation of metal fillers that expand on oxidation and offset the polymer shrinkage. A polymer slurry infiltrates the fibre preform in an evacuated RTM tool and during two curing steps the polymer is converted to a ceramic via pyrolysis.

Sol–gel infiltration has been used to produce CMCs. The sol is a suspension of extremely small particles which gels during drying into a network of large molecules. It can then be sintered to a dense ceramic matrix, at a lower temperature than is necessary for a powder slurry. The cost of this method is fairly high and several infiltration steps are necessary. This technique has been used successfully for some oxide/oxide matrices, for example alumina, zirconia, silica and mullite.

Reaction bonding can at sufficiently high sintering temperatures, typically over 1500°C, result in an almost fully dense matrix without crack formation. It is a method that gives little shrinkage since the reaction product fills the preform. First the preform is infiltrated with a slurry of solid reactants. An in-situ reaction then takes place, usually with a gas reactant forming the ceramic. Si₃N₄ and alumina composites have been formed in this way. This is a good way to achieve high densities of the final product as a volume increase normally is involved in the reaction, leading to an increased infiltration.

Glass matrix composites can also be produced in one step by melt infiltration, but there is a risk of fibre damage at the fairly high temperatures needed. This is a promising technique since it is a quick infiltration technique and only one step is necessary.

DIMOX® is a trade name of a fairly new method of infiltration, involving the oxidation (or nitridation) of molten metals to form the ceramic matrix, so called directed melt oxidation/nitridation. The fibre preform is placed on the melt surface and from the melt surface the ceramic product grows into the preform, giving a well infiltrated, dense preform. The drawback is that there is always a residual trace of metallic phase in the matrix.

Electrophoretic deposition (EPD) is a promising new method that makes complete infiltration into tightly woven fibre preforms possible. It is a simple and inexpensive method. The technique is based on using nanoscale ceramic particles in a stable non-agglomerated form, as for example in a sol or a colloidal suspension. Their net surface electrostatic charge characteristics while in suspension will lead to a migration and deposit of the particles towards an electrode when an electric field is applied. The electrode may be replaced by a conducting fibre preform, to which the particles will be attracted and deposited within, resulting in an effectively infiltrated green body. Oxide/oxide composites prepared
Background

using EPD include for example alumina fibres (Almax) with an alumina matrix\textsuperscript{72,73} and mullite matrix\textsuperscript{74} and Saffil fibres in a mullite matrix.\textsuperscript{75}

Consolidation Methods

Pressureless sintering is seldom used for fibre reinforced ceramic matrix composites due to the difficulties of densifying such microstructures. Usually pressure assisted sintering is used of which there are two types of interest, uniaxial hot pressing (HP) and hot isostatic pressing (HIP). In hot pressing the choice of shape of the composite is limited and there is a risk of variations in density through the sample. Nevertheless HP is the most commonly used consolidation method as it is quick and considerably cheaper than HIP. The HIP technique has a great advantage in that the pressure is isostatic and applied by means of a gas, permitting very complex shapes to be consolidated without shape distortion. A gas, normally argon, transmits the pressure to the powder compact, the so-called green body. The gas must normally be prevented from entering the green body by encapsulating the latter otherwise the pressure would not compact the sample. However, it is possible to HIP a sample without encapsulation if the porosity has been closed by prior sintering, and the method is then called postsinter-HIP in contrast to direct HIP.\textsuperscript{76}

Although metal containers can be used for encapsulation in cases where a low consolidation temperature is sufficient, a glass is usually needed to encapsulate ceramic materials. At high temperatures the glass becomes formable. Different glass types are available depending on the required temperature level. It is important that the glass is soft enough not to crack but viscous enough not to penetrate the body. Most suitable for high temperatures is Vycor\textsuperscript{TM} glass which is an almost pure silica glass while at lower temperatures a borosilicate type of glass, e.g. Pyrex\textsuperscript{TM} is suitable. After enclosing the sample with the glass container it is evacuated at an elevated temperature in order to burn off contamination before sealing. In some cases a powdered glass is applied instead of a container, a method which permits more complex shapes to be densified. The charge must then be heated to a temperature where the glass sinters and becomes gas tight before the gas pressure is applied. It is important to ensure that the glass container does not react chemically with the sample. Silica-containing glass reacts easily with ceramic oxides, especially with alumina forming a mullite reaction product. Often boron nitride or mixtures consisting partly of boron nitride are used as a protective layer between the sample and the glass. A thin molybdenum foil is also sometimes used as protection.

An advantage of HP and HIP densification is that lower sintering temperatures can be used thus limiting grain growth, which is normally a risk when sintering fine grained materials. Fine-grained microstructures will generally exhibit higher strength (but reduced creep resistance) and for transformation toughened zirconia the fine grain size is a prerequisite for necessary control of the transformation process.

A novel rapid consolidation method is spark plasma sintering (SPS). The precursor powder is pressed uniaxially in a carbon die, with an DC voltage applied simultaneously, allowing the sample to be heated extremely fast. Heating rates of up to 600°C per minute have been achieved. Fully dense compacts of for example Si\textsubscript{3}N\textsubscript{4} have been prepared within a few minutes.\textsuperscript{77}
3 MATERIAL

3.1 Oxides

Oxides are important constituents in composites used at high temperatures in air atmosphere due to their inherent oxidation resistance. In contrast, nitrides and carbides and other non-oxides are susceptible to oxidation at higher temperatures. Even though a protective oxidation resistant layer is applied or develops naturally there is risk of composite degradation if the protective layer cracks and oxygen can reach the core of the composite. Corrosion attacks are the main cause of decreased performance of non-oxide composites at elevated temperatures. Several characteristics other than oxidation resistance are clearly required of an oxide if it is to be a candidate constituent in high temperature composites. It must obviously have a high melting point, thermal stability and be phase compatible with the other constituents. For good mechanical performance the elastic modulus generally needs to be high. For high temperature service a high creep resistance is required. The thermal expansions of the constituents should be closely matched to minimise residual stresses. The fracture behaviour of a composite is often an important issue. Properties that directly or indirectly influence fracture are relevant to that behaviour are the crystal structure, the elastic properties, fracture energies and diffusion. These requirements limit the number of possible candidates among the large amount of different oxides. In Table 3.1 oxides with a melting temperature exceeding 1600°C are listed together with certain of their properties. Selected properties are presented in more detail in the sections that follow.

3.1.1 Crystal Structure

The oxides are a group of materials with several different crystal structures, depending on the relative size of the constituent atoms. A feature common to all oxides is the large oxygen anion. The cations being much smaller, fill the interstitial positions of the oxygen lattice. On the basis of the outer symmetry of the crystals, there are seven crystal systems. These are presented in Table 3.2 in terms of the cell constants and the angle between the sides in the unit cell.

There are several structure types in each crystal system some examples being described briefly below.

* Cubic-rock salt*

Ionically bonded metal oxide structures of type AO often have this coordination. The structure consists of a cubic close packed anion lattice in which all octahedral interstitial positions are filled with cations and all of the tetrahedral holes are empty. Both anions and cations have coordination number 6, i.e. they are both octahedrally coordinated. High melting oxides of this type are MgO, NiO, CoO, MnO.

* Cubic-fluorite structure*

Consists of a simple cubic anion lattice with half of the large body-centre interstices occupied by cations. Each cation has eight oxygen nearest neighbours and each oxygen ion is surrounded by 4 cations. Oxides of interest that crystallise in this type are HfO₂, ZrO₂, CeO₂, UO₂, ThO₂.
Table 3.1. Oxides with high-temperature potential.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>(T_m) [°C]</th>
<th>Crystal structure</th>
<th>Density [g/cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>2800</td>
<td>cubic</td>
<td>3.58</td>
</tr>
<tr>
<td>CaO</td>
<td>2580</td>
<td>cubic</td>
<td>3.25-3.38</td>
</tr>
<tr>
<td>NiO</td>
<td>1990</td>
<td>cubic</td>
<td>6.67</td>
</tr>
<tr>
<td>CoO</td>
<td>1935</td>
<td>cubic</td>
<td>6.45</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>cubic</td>
<td>5.43-5.46 (3.7-3.9)</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>1830-1850</td>
<td>tetragonal</td>
<td>4.26</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>2015+/-25</td>
<td>orthorhombic</td>
<td>3.97</td>
</tr>
<tr>
<td>Ti(_2)O(_3)</td>
<td>2130d</td>
<td>trigonal</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>1565</td>
<td>trigonal</td>
<td>5.24</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>-</td>
<td>hexagonal</td>
<td>5.21</td>
</tr>
<tr>
<td>ZnO</td>
<td>1951-2000</td>
<td>hexagonal</td>
<td>3.01</td>
</tr>
<tr>
<td>MgAl(_2)O(_4)</td>
<td>2135</td>
<td>cubic</td>
<td>3.6</td>
</tr>
<tr>
<td>BeO</td>
<td>2530 +/-30</td>
<td>hexagonal</td>
<td></td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>2600</td>
<td>cubic</td>
<td>3.01</td>
</tr>
<tr>
<td>PSZ</td>
<td>2715</td>
<td>cubic</td>
<td>7.13</td>
</tr>
<tr>
<td>UO(_2)</td>
<td>2801-2850</td>
<td>cubic</td>
<td>5.8</td>
</tr>
<tr>
<td>ThO(_2)</td>
<td>3050</td>
<td>cubic</td>
<td></td>
</tr>
<tr>
<td>Y(_2)O(_3)</td>
<td>2401-2450</td>
<td>cubic</td>
<td>9.86</td>
</tr>
<tr>
<td>Mn(_2)O(_4)</td>
<td>1705+/-25</td>
<td>tetragonal</td>
<td>4.86</td>
</tr>
<tr>
<td>BeAl(_2)O(_4)</td>
<td>1870</td>
<td>orthorhombic</td>
<td></td>
</tr>
<tr>
<td>Li(_2)O</td>
<td>&gt;1700</td>
<td>cubic</td>
<td>2.01</td>
</tr>
<tr>
<td>CaCr(_2)O(_4)</td>
<td>2090</td>
<td>cubic</td>
<td>4.8</td>
</tr>
<tr>
<td>Ca(_2)SiO(_4)</td>
<td>2130</td>
<td>monoclinic</td>
<td>3.27</td>
</tr>
<tr>
<td>CaTiO(_3)</td>
<td>1975</td>
<td>cubic (orthorhombic)</td>
<td>4.1</td>
</tr>
<tr>
<td>CaZrO(_3)</td>
<td>2550</td>
<td>monoclinic</td>
<td>4.78</td>
</tr>
<tr>
<td>Ga(_3)O(_3)</td>
<td>1900 (1740)</td>
<td>monoclinic</td>
<td>5.88</td>
</tr>
<tr>
<td>LiAlO(_2)</td>
<td>1900-2000</td>
<td>orthorhombic</td>
<td>2.55</td>
</tr>
<tr>
<td>MgFeO(_4)</td>
<td>1750 +/-25</td>
<td>-</td>
<td>4.44-4.60</td>
</tr>
<tr>
<td>Mg(_2)SiO(_4)</td>
<td>1910</td>
<td>orthorhombic</td>
<td>3.21</td>
</tr>
<tr>
<td>Mn(_3)O(_4)</td>
<td>1705</td>
<td>tetragonal (orthorhombic)</td>
<td>4.86</td>
</tr>
<tr>
<td>Ta(_2)O(_5)</td>
<td>1800</td>
<td>orthorhombic</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 3.2. The seven crystal systems and corresponding cell constants.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Edges and angles of unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>(a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ)</td>
</tr>
<tr>
<td>Orthorhombic (also rhombic)</td>
<td>(a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(a = b \neq c, \alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Trigonal (also rhombohedral)</td>
<td>(a = b = c, \alpha = \beta = \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ)</td>
</tr>
<tr>
<td>Cubic</td>
<td>(a = b = c, \alpha = \beta = \gamma = 90^\circ)</td>
</tr>
</tbody>
</table>


**Materials**

*Cubic-perovskite structure*
This structure is typical for $\text{ABO}_3$ oxides with large A and small B cations. The ideal perovskite structure can be approximated to a cubic close-packed anion lattice where one-fourth of the ions are replaced by a large cation. The smaller highly charged cation occupies one-fourth of the octahedral interstices. The stability of the perovskite structure depends on the relative sizes of the cations and many compounds form distorted perovskite with less symmetry, i.e. orthorhombic or monoclinic arrangement of the anion lattice. Examples of this structure are $\text{SrTiO}_3$, $\text{BaTiO}_3$, $\text{CaTiO}_3$, $\text{SrZrO}_3$, $\text{LaCrO}_3$.

*Cubic-spinel*
The normal spinel consists of a cubic close packed oxygen lattice with divalent metal cation occupying one-eighth of the tetrahedral sites and trivalent metal cations occupying one-half of the octahedral sites.

*Cubic-garnet (YAG)*
A body centred cubic lattice with the large yttrium ions occupying one fourth of the cubic sites. The smaller aluminium ions occupy selected octahedral and tetrahedral sites.

*Orthorhombic*
Mullite is an example of the orthorhombic crystal structure. It is rather complex and often it is projected along the [001] for better understanding, see Figure 3.1.

![Fig. 3.1. Projection of crystal structure of mullite.](image)

*Hexagonal-corundum*
A nearly close-packed anion lattice with cations filling two thirds of the octahedral sites. Examples of oxides with this structure type are $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$.

*Hexagonal-wurtzite*
Metal oxides of class AO and with radius ratios between 0.22 and 0.41 having a strong covalent contribution to bonding are stable in the wurtzite structure. The structure can be described as two hexagonally close-packed interpenetrating lattices. Examples are BeO and ZnO.
Tetragonal-rutile
This consists of a nearly closed packed tetragonal anion lattice where cations occupy half of the octahedral sites. An oxide of this crystal type is TiO₂.

3.1.2 Thermal Properties

The thermal properties of oxides are significant in applications where resistance to thermal shock is important, or where there are requirements with respect to thermal insulation or conductivity properties. Knowing the thermal expansion of the constituents is the key to minimising residual stresses after production.

Thermal expansion

The thermal expansion coefficient of an oxide is related both to the bond strength and the crystal structure. Oxides with mainly ionic bonding have larger coefficients of thermal expansion than oxides with a higher degree of covalent bonding. Oxides with close atomic packing have larger thermal expansion. Silica has a very open crystal structure, which leads to a very low coefficient of thermal expansion. The vibration of the lattice due to increasing temperature can be taken care of in the structure by for example adjustment of bond angle.²⁹

Apart from its obvious influence on dimensional variability, thermal expansion affects the thermal shock behaviour. In multiphase materials it has far-reaching significance since thermal expansion mismatch between phases creates local residual stress fields in the microstructure in response to temperature changes which in turn influences mechanical behaviour and particular fracture behaviour.⁹ In fact, similar effects can be expected in polycrystalline, single phase materials if the phase exhibits anisotropy of thermal expansion and/or elastic properties with respect to crystal orientation.⁸⁰ In general, the local residual stress associated with a representative grain in a polycrystal will increase with the degree of anisotropy and elastic stiffness.

Thermal expansion is commonly measured on bulk samples using dilatometry. However, an alternative method is to use high temperature X-ray diffraclometry. The latter method has the advantage that it yields expansion curves for specific crystallographic directions which is useful, for example, in assessing residual internal stress effects in polycrystals.

The X-ray diffractionmetry can be performed on bulk material or on powder. In general, these will not yield identical results since in bulk polycrystals, individual grains will be constrained by the surrounding grains while in powders they will generally be less constrained. In Paper II values of expansion coefficients corresponding to random polycrystals have been derived from X-ray diffraction data using the expression:

\[ \alpha = (\alpha_1 + \alpha_2 + \alpha_3)/3 \]  

[3.1]

where \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) are the thermal expansion coefficients in three mutually perpendicular directions in the crystal lattice.

The coefficients of thermal expansion of some polycrystal and single crystal oxides are given in Table 3.3 and Table 3.4.
Table 3.3. Average thermal expansion coefficients of oxides. (Various sources listed in reference 81).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\alpha (20-500^\circ C)$ ($K^{-1}$) ($\times 10^{-6}$)</th>
<th>$\alpha (20-1000^\circ C)$ ($K^{-1}$) ($\times 10^{-6}$)</th>
<th>$\alpha (20-1500^\circ C)$ ($K^{-1}$) ($\times 10^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>6.9</td>
<td>9.0</td>
<td>14.2</td>
</tr>
<tr>
<td>MgO</td>
<td>12.9</td>
<td>14.2</td>
<td>16.1</td>
</tr>
<tr>
<td>SrO</td>
<td>12.4</td>
<td>13.5</td>
<td>16.1</td>
</tr>
<tr>
<td>HiO$_3$</td>
<td>-</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>ThO$_3$</td>
<td>7.1</td>
<td>9.4</td>
<td>10.7</td>
</tr>
<tr>
<td>ZrO$_2$, monoclinic</td>
<td>7.1</td>
<td>7.7</td>
<td>-</td>
</tr>
<tr>
<td>2Y-ZrO$_2$ (t)</td>
<td>10</td>
<td>10.5</td>
<td>11.0</td>
</tr>
<tr>
<td>2.8Y-ZrO$_2$ (t)</td>
<td>10.2</td>
<td>10.5</td>
<td>11.0</td>
</tr>
<tr>
<td>12Y-ZrO$_2$ (c)</td>
<td>9.2</td>
<td>9.6</td>
<td>11.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.024</td>
<td>8.468</td>
<td>8.907</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>9.93</td>
<td>7.34</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$SiO$_5$ (3A.2S)</td>
<td>-</td>
<td>5.37</td>
<td>-</td>
</tr>
<tr>
<td>LaCrO$_3$ (L.C)*</td>
<td>8.1</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td>SrZrO$_3$ (S.Z)</td>
<td>9.33</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>Y$_2$Al$_2$O$_7$ (3Y.5A)</td>
<td>-</td>
<td>8.6</td>
<td>-</td>
</tr>
</tbody>
</table>

* Magnesia stabilised

Table 3.4. Thermal expansion in specific crystallographic directions (20° - 1000°C unless otherwise indicated).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\alpha (K^{-1})(\times 10^{-6})$</th>
<th>$\alpha (K^{-1})(\times 10^{-6})$</th>
<th>$\alpha (K^{-1})(\times 10^{-6})$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.2</td>
<td>8.2</td>
<td>8.98</td>
<td>82</td>
</tr>
<tr>
<td>Al$_2$SiO$_5$ (3A.2S)</td>
<td>3.98*</td>
<td>6.58*</td>
<td>5.56</td>
<td>Own data</td>
</tr>
<tr>
<td>Y$_2$Al$_2$O$_7$ (2Y.A)</td>
<td>12.5</td>
<td>7.2</td>
<td>3.1</td>
<td>83</td>
</tr>
</tbody>
</table>

*Sensitive to the state of mullite and can exhibit changeover

**Thermal conductivity**

Ceramics in general have very low thermal conductivity compared to metals, with the exception of beryllia (BeO). The reason for this is that ceramics lack free electrons and heat is conducted through the lattice mainly in the form of phonons (lattice vibrations). The phonons easily interact with imperfections in the crystal structure which leads to a reduction of the mean free path. To achieve a high thermal conductivity the oxide should have a simple composition and structure, be close-packed and have high purity. For example, Al$_2$O$_3$ or MgO have higher heat conductivities than MgAl$_2$O$_4$ (magnesium aluminate spinel) due to the more complex structure of the latter. Mullite (3Al$_2$O$_3$·2SiO$_2$) has a lower thermal conductivity than the spinel. Glasses and amorphous ceramics show lower conductivities than crystalline materials, in accordance with their disordered structure. Thermal conductivity decreases with temperature (zirconia is an exception in this respect) due to increased scattering of the phonons, up to a temperature level where radiant heat transfer starts to take over. This makes it important to quote the temperature with the value of the thermal conductivity. Porosity affects the thermal conductivity very much.

Thermal conductivity as well as thermal expansion is one of the factors that determines the resistance of a material to thermal shock. In Table 3.5 values of thermal conductivity for some fully dense oxides are shown.
Materials

Table 3.5. Thermal conductivity of oxides. (Various sources listed in reference 81).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Thermal conductivity at room temperature (Wm⁻¹K⁻¹)</th>
<th>Thermal conductivity at 1000°C (Wm⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>300</td>
<td>18</td>
</tr>
<tr>
<td>MgO</td>
<td>40</td>
<td>7</td>
</tr>
<tr>
<td>ThO₂</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>UO₂</td>
<td>12</td>
<td>3.2</td>
</tr>
<tr>
<td>ZrO₂ (pure)</td>
<td>1.8;6(98%)</td>
<td>2.2;3.6</td>
</tr>
<tr>
<td>ZrO₂₋58%Y₂O₃</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>38</td>
<td>7</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Al₂MgO₄ (A.M)</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>Al₂SiO₅₁₃ (3A,2S)</td>
<td>6.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Y₂Al₅O₁₁(3Y:5A)</td>
<td>8.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

3.1.3 Elastic Properties

The elastic properties of composite constituents greatly affect the mechanical behaviour of the composite, for example fracture toughness and tensile strength. Young’s modulus increases with bond strength and consequently oxides with high proportions of covalent bonding have the highest values of elastic modulus. In general the elastic moduli decrease approximately linearly with temperature. For the high melting point oxides of interest here the decrease is around 20% up to 1500°C. The Poisson ratio should normally not change significantly with temperature.

Elastic properties are relatively difficult to measure. Conventional load/deformation testing can be applied to polycrystals but the results are sensitive to porosity and precise strain measurement is difficult. An alternative is to determine the elastic constants of single crystals by dynamic methods and from these derive the elastic properties of a polycrystal as an aggregate of single crystals with defined orientation distributions. Good approximations are obtained based on the upper and lower bounds by Voigt and Reuss and Hashin-Strikhman. In Table 3.6 single crystal Young’s moduli are listed and in Table 3.7 the corresponding aggregate properties are given. It is also possible to derive Poisson’s ratio for aggregates and the values are given in Table 3.7. Elastic anisotropy of cubic crystals expressed as \(2(S_{11}-S_{12})/S_{44}\), where \(S_{ij}\) are the elastic compliance constants of the single crystal is also listed. A large deviation of the anisotropy factor from unity indicates a high anisotropy. Such anisotropy leads to variations in stress from grain to grain in a polycrystal and can therefore be a source of low strength but also in favourable circumstances to improved toughness.

In the absence of reliable experimental values of elastic modulus correlations can be sought with other properties such as lattice energy, i.e. the total energy required to completely separate the ions in the lattice. The lattice energy is a thermodynamic property which can be found for many oxides in standard reference works. The reasonably good correlation between \(E\) and lattice energy is demonstrated in Figure 3.2.

32
Table 3.6. Young’s moduli of single crystals derived from single crystal elastic data. (Various sources listed in reference 81).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Crystal structure</th>
<th>$E_{100}$</th>
<th>$E_{110}$</th>
<th>$E_{111}$</th>
<th>Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>cubic</td>
<td>245</td>
<td>308</td>
<td>336</td>
<td>1.49</td>
</tr>
<tr>
<td>MgO(1473K)</td>
<td>cubic</td>
<td>166</td>
<td>251</td>
<td>302</td>
<td>2.13</td>
</tr>
<tr>
<td>SrO₂</td>
<td>cubic</td>
<td>142</td>
<td>143</td>
<td>143</td>
<td>1.01</td>
</tr>
<tr>
<td>UO₂</td>
<td>cubic</td>
<td>339</td>
<td>199</td>
<td>175</td>
<td>0.47</td>
</tr>
<tr>
<td>UO₩₃</td>
<td>cubic</td>
<td>252</td>
<td>133</td>
<td>115</td>
<td>0.41</td>
</tr>
<tr>
<td>CoO</td>
<td>cubic</td>
<td>155</td>
<td>197</td>
<td>217</td>
<td>1.45</td>
</tr>
<tr>
<td>spinel (MgAl₂O₄)</td>
<td>cubic</td>
<td>171</td>
<td>284</td>
<td>364</td>
<td>2.43</td>
</tr>
<tr>
<td>spinel (MgO-3.5Al₂O₃)</td>
<td>cubic</td>
<td>196</td>
<td>307</td>
<td>377</td>
<td>2.16</td>
</tr>
<tr>
<td>spinel (MgO-2.6Al₂O₃)</td>
<td>cubic</td>
<td>194</td>
<td>304</td>
<td>375</td>
<td>2.18</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>cubic</td>
<td>303</td>
<td>546</td>
<td>746</td>
<td>3.67</td>
</tr>
<tr>
<td>ThO₂</td>
<td>cubic</td>
<td>319</td>
<td>230</td>
<td>210</td>
<td>0.61</td>
</tr>
<tr>
<td>YAG</td>
<td>cubic</td>
<td>279</td>
<td>284</td>
<td>286</td>
<td>1.03</td>
</tr>
<tr>
<td>MnO</td>
<td>cubic</td>
<td>139</td>
<td>182</td>
<td>202</td>
<td>1.53</td>
</tr>
<tr>
<td>SrO</td>
<td>cubic</td>
<td>142</td>
<td>143</td>
<td>143</td>
<td>1.01</td>
</tr>
<tr>
<td>ZrO₂, 0 mol% Yttria</td>
<td>monoclinic</td>
<td>391</td>
<td>156</td>
<td>130</td>
<td>0.28</td>
</tr>
<tr>
<td>YSZ, 8.1 mol% Y₂O₃</td>
<td>cubic</td>
<td>365</td>
<td>179</td>
<td>153</td>
<td>0.36</td>
</tr>
<tr>
<td>YSZ, 11.1 mol% Y₂O₃</td>
<td>cubic</td>
<td>362</td>
<td>190</td>
<td>164</td>
<td>0.40</td>
</tr>
<tr>
<td>YSZ, 12.1 mol% Y₂O₃</td>
<td>cubic</td>
<td>362</td>
<td>195</td>
<td>169</td>
<td>0.41</td>
</tr>
<tr>
<td>YSZ, 15.5 mol% Y₂O₃</td>
<td>cubic</td>
<td>351</td>
<td>203</td>
<td>178</td>
<td>0.46</td>
</tr>
<tr>
<td>YSZ, 17.9 mol% Y₂O₃</td>
<td>cubic</td>
<td>341</td>
<td>210</td>
<td>186</td>
<td>0.50</td>
</tr>
<tr>
<td>BeO</td>
<td>hexagonal</td>
<td>397</td>
<td>397</td>
<td>401</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>hexagonal</td>
<td>127</td>
<td>127</td>
<td>124</td>
<td>-</td>
</tr>
<tr>
<td>Ba₂TiO₅</td>
<td>hexagonal</td>
<td>122</td>
<td>122</td>
<td>145</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂(RT)</td>
<td>tetragonal</td>
<td>148</td>
<td>148</td>
<td>356</td>
<td>-</td>
</tr>
<tr>
<td>ZrSiO₄(RT)</td>
<td>tetragonal</td>
<td>127</td>
<td>127</td>
<td>222</td>
<td>-</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>tetragonal</td>
<td>138</td>
<td>138</td>
<td>222</td>
<td>-</td>
</tr>
</tbody>
</table>

### 3.1.4 Creep

Creep resistance tends to decrease with the proportion of ionic bonding in the oxide, because ionic bonding is weaker. In most glass-free polycrystalline oxides diffusion creep predominates. This involves the migration of vacancies down a gradient from grain boundaries experiencing tensile stresses to boundaries undergoing compression; simultaneously atoms move in the opposite direction leading to elongation of the grains and the test bar. Grain size is important in diffusion creep, partly because the grain size determines the distance atoms have to diffuse and partly because the grain boundary provides an alternative diffusion path. Thus two diffusion paths can be considered: bulk diffusion through the body of the crystal, leading to so called Nabarro–Herring creep and diffusion along the grain boundary leading to Coble creep.

In contrast to diffusion creep the mechanism in single crystals is the movement of dislocations through the crystal structure. Such movement is accommodated by slip along preferential crystal planes. For measurable creep of a single crystal to occur, dislocations must
be present or created and then start moving. Defects in the lattice structure decrease creep by pinning dislocations.\textsuperscript{87}

Creep in glasses is controlled by viscous flow and is a function of the viscosity of the glass at the temperature of interest. The viscous flow of glasses is an important mechanism of creep in many commercial polycrystalline ceramics including oxides since these often contain secondary glass phases at the grain boundary.\textsuperscript{91}

**Table 3.7.** Aggregate elastic moduli and Poisson’s constants derived from single crystal data. (Various sources listed in reference 81).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Crystal structure</th>
<th>$E_{\text{upper}}$</th>
<th>$E_{\text{lower}}$</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>cubic</td>
<td>297</td>
<td>298</td>
<td>0.25</td>
</tr>
<tr>
<td>MgO(1473K)</td>
<td>cubic</td>
<td>238</td>
<td>242</td>
<td>0.18</td>
</tr>
<tr>
<td>SrO$_2$</td>
<td>cubic</td>
<td>142</td>
<td>142</td>
<td>0.17</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>cubic</td>
<td>233</td>
<td>228</td>
<td>0.21</td>
</tr>
<tr>
<td>UO$_{1,71}$</td>
<td>cubic</td>
<td>162</td>
<td>157</td>
<td>0.32</td>
</tr>
<tr>
<td>CoO</td>
<td>cubic</td>
<td>190</td>
<td>190</td>
<td>0.33</td>
</tr>
<tr>
<td>spinel (MgAl$_2$O$_4$)</td>
<td>cubic</td>
<td>269</td>
<td>276</td>
<td>0.27</td>
</tr>
<tr>
<td>spinel (MgO-3.5Al$_2$O$_4$)</td>
<td>cubic</td>
<td>291</td>
<td>296</td>
<td>0.26</td>
</tr>
<tr>
<td>spinel (MgO-2.6Al$_2$O$_4$)</td>
<td>cubic</td>
<td>289</td>
<td>294</td>
<td>0.26</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>cubic</td>
<td>521</td>
<td>557</td>
<td>0.0</td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>cubic</td>
<td>250</td>
<td>249</td>
<td>0.28</td>
</tr>
<tr>
<td>YAG</td>
<td>cubic</td>
<td>283</td>
<td>283</td>
<td>0.25</td>
</tr>
<tr>
<td>MnO</td>
<td>cubic</td>
<td>174</td>
<td>175</td>
<td>0.31</td>
</tr>
<tr>
<td>SrO</td>
<td>cubic</td>
<td>142</td>
<td>142</td>
<td>0.21</td>
</tr>
<tr>
<td>ZrO$_2$, 0 mol% Yttria</td>
<td>monoclinic</td>
<td>218</td>
<td>200</td>
<td>0.32</td>
</tr>
<tr>
<td>YSZ, 8.1 mol% Y$_2$O$_3$</td>
<td>cubic</td>
<td>226</td>
<td>217</td>
<td>0.31</td>
</tr>
<tr>
<td>YSZ, 11.1 mol% Y$_2$O$_3$</td>
<td>cubic</td>
<td>232</td>
<td>225</td>
<td>0.31</td>
</tr>
<tr>
<td>YSZ, 12.1 mol% Y$_2$O$_3$</td>
<td>cubic</td>
<td>236</td>
<td>229</td>
<td>0.31</td>
</tr>
<tr>
<td>YSZ, 15.5 mol% Y$_2$O$_3$</td>
<td>cubic</td>
<td>239</td>
<td>234</td>
<td>0.31</td>
</tr>
<tr>
<td>YSZ, 17.9 mol% Y$_2$O$_3$</td>
<td>cubic</td>
<td>241</td>
<td>238</td>
<td>0.30</td>
</tr>
<tr>
<td>BeO</td>
<td>hexagonal</td>
<td>398</td>
<td>398</td>
<td>0.20</td>
</tr>
<tr>
<td>ZnO</td>
<td>hexagonal</td>
<td>124</td>
<td>124</td>
<td>0.36</td>
</tr>
<tr>
<td>TiO$_2$(RT)</td>
<td>tetragonal</td>
<td>316</td>
<td>259</td>
<td>0.26-0.30</td>
</tr>
<tr>
<td>ZrSiO$_4$(RT)</td>
<td>tetragonal</td>
<td>210</td>
<td>187</td>
<td>0.33-0.35</td>
</tr>
<tr>
<td>Be$_2$Al$_2$Si$_2$O$_9$</td>
<td>hexagonal</td>
<td>211</td>
<td>211</td>
<td>0.26</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>trigonal/hexag.</td>
<td>408</td>
<td>397</td>
<td>0.23</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>trigonal</td>
<td>94</td>
<td>96</td>
<td>0.08</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>tetragonal</td>
<td>194</td>
<td>165</td>
<td>0.33-0.31</td>
</tr>
</tbody>
</table>
3.2 Fibres

A key issue in improving the performance of fibre reinforced ceramic composites is the fibre reinforcement. Much ongoing research has the aim of increasing the performance of fibres, especially under thermal exposure. The processing of a ceramic material in the form of a filament differs significantly from those used for the production of bulk material. Fibre processing is not only expensive, but is also extremely delicate because the processing determines the properties obtained in the final product.

There are two families of fibres used as reinforcement in composites; non-oxide fibres and oxide fibres. Non-oxide fibres, especially SiC-based possess a higher strength at room temperature, but degrade rapidly at temperatures above 1100°C in air. Therefore, in applications in air oxide fibres, mainly alumina based, are chosen due to their inherent oxidation stability. Single crystal oxide fibres attain the highest creep resistance possible but their main drawback is their extremely high cost. Development is ongoing to find attractive
candidates among polycrystalline oxide fibres. The main strategies are to develop a microstructure with grains elongated in the fibre axial direction or to find new multiphase oxides, with increased resistance to creep and increased microstructural stability at high temperature.

3.2.1 Oxide Fibres

Available oxide fibres have traditionally been based mainly on alumina. The first small diameter continuous oxide fibre was the $\alpha$-alumina FP fibre developed by DuPont in the late 70s. The fibre produced was 20 micron in diameter and consisted of 0.5 micron $\alpha$-alumina grains. The FP fibre retained its strength to 1000°C. Above this temperature the fibre started to degrade mainly by grain growth. PRD-166, a modification of the FP fibre, contained 15-20 wt% yttria-stabilised zirconia. The zirconia grains were only 0.1 microns in diameter and inhibited grain growth in the alumina as well as increasing creep resistance. These fibres are however not currently in production. Another $\alpha$-alumina fibre is the Almax fibre having a diameter of 10 microns, which allows it to be woven.

The fibre Nextel™ 610 produced by the company 3M has a diameter of 10 microns and is based on $\alpha$-alumina but with a small amount of $\text{Fe}_2\text{O}_3$ and $\text{SiO}_2$ added as a nucleating agent and grain growth inhibitor respectively. The grain size is very small, only about 0.1 microns and this leads to a high strength (about 2900MPa) but poor creep resistance. The strength is reduced at temperatures above 1000°C due to grain growth.

There are other fibres in the Nextel family based on a mullite composition ($\text{Al}_2\text{O}_3$-$\text{SiO}_2$), such as Nextel 310, Nextel 440 and Nextel 550. These fibres contain boria ($\text{B}_2\text{O}_3$) to restrict grain growth and are limited to application temperatures below 1000°C.

Nextel 720 is an important fibre because of its higher temperature stability relative to the other Nextel fibres. Nextel 720, produced by a sol-gel process and having a composition of 85 wt% $\text{Al}_2\text{O}_3$ - 15 wt% $\text{SiO}_2$, is richer in alumina than other Nextel fibres, but with a small percentage of silica added in order to prevent grain growth of alumina. The microstructure consists of a mixture of alumina and mullite grains. The alumina grains have diameters of approximately 0.1 $\mu$m. These are distributed among larger (0.5 $\mu$m) mullite grains consisting of many smaller subgrains. The creep resistance of Nextel 720 is superior to that of previous Nextel fibres and this is thought to be partly due to the higher creep resistance of mullite and partly to the microstructural morphology described above.

The diameter of the fibre is 10-12 $\mu$m which allows weaving. According to the manufacturer, the tensile strength of the fibre is 2.1 GPa at room temperature (gauge length 51 mm). Milz et al. made a Weibull evaluation of 30 Nextel 720 fibres and obtained a Weibull modulus of 4.8 while a value of 7.6 is quoted by the manufacturer. The thermal expansion is $6.0 \times 10^{-6}$ K$^{-1}$ between 100-1100°C.

Thermal degradation of the fibres has been studied by Delégis et al. The authors report that large $\alpha$-alumina platelets (1.5 microns) formed on the surface as a result of heat-treatments above 1200°C. However, it was found that for 5h exposure the heat-treatment temperature must exceed 1400°C for a significant loss in tensile strength to occur. On the other hand, Petry and Mah found a 9% strength loss after an exposure at 1100°C for 2 hours. Among possible degradation mechanisms they suggest thermal grooving, grain growth and /or annealing of the mullite subgrain boundaries. Milz et al. report a severe degradation in fibre strength after heat-treatment at 1300°C (2 hours). They suggest that the strength degradation is due to locally enriched impurities, which in their test had greater significance since they used a larger gauge length. In many application the presence of a silicon containing phase as in Nextel 720 is not desirable due to the sensitivity to for example alkali metals.
The latest member of the Nextel family is Nextel 650 having a composition Al\(_2\)O\(_3\) + 10 wt% ZrO\(_2\) + 1 wt% Y\(_2\)O\(_3\) and an average diameter of 11 \(\mu\)m. The alumina grains are equiaxed with a diameter of about 0.1 \(\mu\)m. The ZrO\(_2\) exists as 5–10 nm particles within the grains and 20–30 nm particles at the grain boundary triple points. The fibre is doped with rare earth metals and exhibit good creep resistance even superior to Nextel 720. Earlier studies of bulk alumina have demonstrated that small additions (a few hundred ppm) of rare earth metals segregate at grain boundaries and lead to an associated improved creep resistance presumably due to inhibition of grain boundary creep processes. However, these material had a coarser grain size, around 1 \(\mu\)m, which probably explains the need of higher doping levels in the finer grained fibre. The rare earth dopants were found to lead to grain coarsening above 1400°C leading to a reduction in strength. The ZrO\(_2\) addition was made to reduce the grain growth and did not lead to a significant loss of creep resistance.

The phases present in the fibre are \(\alpha\)-alumina and cubic zirconia. No tetragonal zirconia was found by XRD which implies that there is probably no transformation toughening. The strength of the fibres is high (2.4–2.7MPa). At 1400°C the fibres had a retained strength of over 60% to be compared with Nextel 610 and 720 that retained 30% and 85% of their room temperature strength respectively. Table 3.8 compares some properties of the three most interesting Nextel fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Strength [GPa]</th>
<th>Young’s modulus [GPa]</th>
<th>Density [g/cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nextel 610</td>
<td>3.3</td>
<td>373</td>
<td>3.88</td>
</tr>
<tr>
<td>Nextel 720</td>
<td>2.1</td>
<td>260</td>
<td>3.4</td>
</tr>
<tr>
<td>Nextel 650</td>
<td>2.4–2.7</td>
<td>350</td>
<td>4.1</td>
</tr>
</tbody>
</table>

A number of single crystal oxide fibres are or have been available, the first one being the Saphikon™ single crystal alumina fibre. These fibres are grown from molten alumina using the edge-defined film fed growth (EFG) technique. Their diameter is approximately 125 microns, but with large variations between different batches. The fibre has a tensile strength of over 3.5 GPa at room temperature (L=25.4 mm) which is substantially higher than polycrystalline alumina fibres. However, a fall in strength at low temperatures (300°C) with a subsequent recovery at higher temperature has been observed. The large diameter together with the slow production rate lead to the high cost of these fibres. The seed crystal needs to be carefully oriented in the c-axis direction, because even a small deviation leads to a reduction in creep properties. At high temperatures and slow strain rates slow crack growth can be a problem for the Saphikon fibres.

More complex single crystal fibres have been produced. For example yttrium aluminium garnet (YAG, Y\(_3\)Al\(_5\)O\(_{12}\)) fibres have been produced and shown to have less dependence on orientation than the sapphire fibres. Single crystal spinel fibres also show less orientation dependence implying that composites with these fibres will be less sensitive to off-axis loading. The tensile strength of the spinel fibres (2.14 GPa) is somewhat lower than that of the c-axis sapphire due to a strong tendency for facetting on the fibre surfaces. The strength retention of the YAG fibre is comparable to that of the c-axis alumina fibres, but the room temperature tensile strength is much lower.

Single crystal mullite fibres have been produced by the Laser-Heated Floating Zone (LHFZ) method. The mullite fibres exhibit superior strength retention (80% of their RT strength at 1450°C). McClellan et al. reported that [001] Y\(_2\)O\(_3\)-stabilised


ZrO₂ fibres grown by the LHFZ technique exhibit a much higher thermal expansion coefficient than other oxide fibres but exhibited excellent strength retention at elevated temperatures. However, like the YAG fibre they had a relatively low tensile strength at room temperature. The poor tensile strength of these fibres has been attributed to faceting on fibre surfaces and the presence of surface defects associated with the fibre growth conditions. The fibre growth conditions must be improved to eliminate the strength-limiting defects in order to increase their high temperature strength.

Successful attempts have been made to produce single crystal fibres from oxide/oxide eutectics with a fibrous or lamellar microstructure. Ceramic eutectics with aligned structures have good compatibility and bonding between phases and they are free from transverse grain boundaries which limit rupture strength. Moreover, the two-phase structure precludes the formation of macroscopic facets on fibre surfaces, which are frequently the source of strength limiting flaws in single crystal fibres as mentioned above. Directionally solidified Al₂O₃ / YAG eutectic fibres having a lamellar structure (the YAG phase distributed uniformly in the Al₂O₃ phase) oriented parallel to the fibre axis; they showed improved stress-rupture resistance up to 1300°C compared to c-axis sapphire fibres. The fibre strength is not degraded at high temperatures as much as that of single phase alumina fibres. The aligned nature of the two phases is believed to inhibit movement in the microstructure and thus lead to the high creep resistance. The current available monofilament have large diameters (150–300 microns) and also here the slow production rate leads to high costs.

A eutectic fibre of Al₂O₃/ZrO₂(Y₂O₃) has also been grown by the EFG technique. The average tensile strength of the fibre with a diameter of 125 microns is 1.2 GPa, which is fairly low compared to c-axis alumina, but the strength retention at elevated temperatures is better. The creep resistance is lower than that of c-axis sapphire fibres, but is not as sensitive to off-axis loading. The stability of fine lamellar structure in YAG/alumina eutectic fibres at elevated temperatures has been investigated by Park et al. Significant coarsening of the fine lamellar structure in both fibres was observed, the driving force for the coarsening presumably being the associated reduction in interfacial energy.

Reported tensile creep data for alumina-based fibres has been collected and compared by means of a Larson–Miller evaluation. Table 3.9 gives some details of the fibres and Figure 3.3 shows a L–M plot. It can be seen that by far the best creep resistance is achieved by single crystal fibres. Interesting to note is that spinel is superior to sapphire. Nextel 720 fibres with a second phase of mullite have superior creep resistance to other polycrystalline fibres. Nevertheless, polycrystalline alumina–based fibres are generally limited to applications below 1200°C. As described above research is currently in progress to design the microstructure of polycrystalline oxide fibres in order to limit creep. The YAG–alumina eutectic fibre from Saphikon with its oriented, lamellar microstructure shows promising creep properties. It has been found that fibre creep data is rather well correlated to creep of the same material with the same microstructure in bulk form. L–M plots for bulk oxides have been presented in Antti and Warren while Deng and Warren have reviewed data for several single crystal oxides. A nice review of fibres in general is given by reference.
Table 3.9. Selected alumina-based fibres and some of the properties. (Various sources listed in reference 81).

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Composition</th>
<th>Diam [µm]</th>
<th>Mean fracture strength [MPa]</th>
<th>Weibull modulus</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre FP</td>
<td>α-alumina</td>
<td>20</td>
<td>1200</td>
<td>5 (L=198mm)</td>
<td></td>
</tr>
<tr>
<td>Almax</td>
<td>α-alumina</td>
<td>10</td>
<td>1020</td>
<td></td>
<td>Can be woven</td>
</tr>
<tr>
<td>PRD-166</td>
<td>Al₂O₃, 15-25 ZrO₂</td>
<td>20</td>
<td>1460</td>
<td>3-4 (L=17mm)</td>
<td></td>
</tr>
<tr>
<td>Sapphire</td>
<td>Sapphire</td>
<td>130</td>
<td>2650*</td>
<td>6*</td>
<td>Single crystal</td>
</tr>
<tr>
<td>(Saphikon Inc.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nextel 610</td>
<td>α-alumina</td>
<td>12</td>
<td>1900</td>
<td></td>
<td>Grain size 0.1 µm</td>
</tr>
<tr>
<td>Nextel 720</td>
<td>85 Al₂O₃, 15 SiO₂</td>
<td>12</td>
<td>2100 (L=25mm) 1200 (L=50mm)</td>
<td></td>
<td>2-phase, alumina/mullite</td>
</tr>
<tr>
<td>Spinel</td>
<td>MgAl₂O₄</td>
<td></td>
<td></td>
<td></td>
<td>Single crystal [110]</td>
</tr>
<tr>
<td>YAG-alumina</td>
<td>YAG-Al₅O₃</td>
<td>140</td>
<td>1350 (L=60mm)</td>
<td></td>
<td>Lamellar microstructure</td>
</tr>
<tr>
<td>(Saphikon Inc.)</td>
<td>eutectic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Own results

Fig. 3.3. Larson-Miller plot for selected polycrystalline and monocrystalline fibres where \( t \) refers to time to reach a strain of \( 10^{-5} \) at the observed steady state creep rate.
3.2.2 Fibres in This Study

The first part of this thesis, involving two production techniques for all-oxide composites using Saphikon sapphire fibres, see section about dip coating (section 4.1) and tube cladding (section 4.2) below and Paper I. The second part, concerning the mechanical properties of all-oxide composites involved both Saphikon fibres (Paper VI) and Nextel 720 fibres (Paper III, IV and V).

3.3 Composites in This Study

3.3.1 Previous Research on Sapphire/Alumina Composites

Sapphire fibre reinforced alumina is a thermodynamically stable system which has attracted much interest for use in severe conditions. As both constituents are of the same material the composite exhibits little thermal expansion mismatch, which minimises processing damage and degradation due to thermal shock. The fibre/matrix interface plays a vital role and several different oxides have been investigated as possible candidates. However, there are not many suitable oxides due to the amphoteric nature of alumina, i.e. it can react with both basic and acidic oxides. Mixed aluminates that are compatible with alumina and that have crystallographic planes of easy cleavage, which promote crack deflection, are the β-alumina-magnetoplumbites. However, with this interphase fibre degradation has been found to occur due to morphological instability of the interface and fibre growth into the matrix. Other oxide compounds with inherent weakness that have attracted interest are the rare-earth phosphates, for example monazite (LaPO$_4$). However, compatibility is only valid for stochiometric monazite; if there is an excess of La or P reaction with alumina occurs which could well lead to a degradation of fibre strength.

Barium zirconate, BaZrO$_3$, has been identified as a possible interphase material for alumina fibres/alumina matrix composites. During processing the alumina and barium zirconate reacted to form a series of layers, which led to crack deflection. Fugitive fibre coating has been tested with Saphikon fibres, molybdenum and carbon coated fibres having been proposed. The load transfer is dependent on the degree of fibre surface roughness. The drawbacks of fugitive coatings are poor transverse properties and the risk of local fibre/matrix reactions at contact points. A combination of an inner layer of a fugitive coating and an outer layer of zirconia has been reported by Sudre et al. After processing the carbon was oxidised away leaving a gap between the fibre and the zirconia interphase. The composite showed desirable behaviour in flexural and tensile testing.

Zirconium dioxide is chemically compatible with alumina but it has been shown that a dense zirconia interphase between sapphire fibres and the alumina matrix is not suitable for optimising composite toughness and strength, due to too high interfacial shear strength and interfacial friction. One solution to this is to use a zirconia interphase containing microporosity. Porous zirconia interphases have been obtained successfully by coating the fibres with a carbon/zirconia mixture; after burn-out of the carbon from the consolidated composites a porous zirconia interface remains. Lundberg and Eckerbom studied model composites with porous zirconia coated sapphire fibres in an alumina matrix and documented crack deflection at the interphase. It was also shown by Davis et al. that the zirconia interphase must be porous in order to be sufficiently weak. The fracture energy of the sapphire/zirconia interface was too high ($\Gamma_i/\Gamma_f$ = 0.8) to satisfy the debonding criterion but debonding could be encouraged by development of a porous microstructure which provided a lower energy fracture path through the coating ($\Gamma_i/\Gamma_f$ < 0.25) which is a prerequisite for
debonding due to Evans, He and Hutchinson. The interfacial shear strength of a zirconia coated sapphire fibre has been shown to decrease with increasing fibre coating thickness (from 389 to 241 MPa for 0.15 of 1.45 micron thick coatings respectively). No effect of fibre coating thickness on the interfacial sliding stress was observed.

The properties have been thoroughly investigated of sapphire reinforced alumina as a possible material for combustor tiles. Zirconia coated sapphire fibres in a hot-pressed alumina matrix experienced crack deflection both at the sapphire/zirconia interface and within the zirconia interphase. Lewis et al. have documented a fracture stress in bending of almost 500 MPa at a strain to failure of about 0.25% in a fibre reinforced alumina matrix the fibres being coated with porous zirconia. The stress-strain response was pseudo-ductile with limited pull-out. The debond stress in a push-out test was 14 MPa and the sliding stress was about 11 MPa. A later study of a similar composite but with an interface of in-situ reacted β-alumina yielded 120 MPa and 45 MPa respectively for the corresponding parameters.

The stress-strain response of a composite with monazite coated sapphire fibres in an alumina matrix has been investigated by Marshall et al. The flexure strength was almost 150 MPa and fracture surfaces showed fibre debonding and sliding.

Reaction bonding of the matrix using an alumina/aluminium mixture has been shown to be a successful alternative for production of sapphire fibre reinforced alumina. The compaction of the alumina powder is improved and leads to a defect-free structure of the matrix. At temperatures below 1300°C the composites with uncoated sapphire fibres show crack deflection and fibre/matrix debonding due to differences in elastic constants and high applied stresses. However, at temperatures above 1300°C a coating is necessary on the fibres. The use of Al,TiO₃ as an interface obtained by coating the fibres with Ti- or Ti/Al shows promise. Reaction bonding of the matrix in combination with a porous zirconia coating has also been reported. With the addition of aluminium, the theoretical density of the alumina matrix was increased from 62% up to 85%. Both first matrix cracking and the UTS increased significantly. A UTS of over 350 MPa was achieved in bending.

### 3.3.2 Previous Research on Nextel 720/AS Composites

The tensile strength of a Nextel 720/AS composite has been reported to be 171 MPa at room temperature and 149 MPa at 1000°C. The same author reports the trans-thickness strength to be approximately 2.8 MPa. Jurf and Butner reported a very small difference in strength between room temperature and 1000°C, 179 MPa and 170 MPa respectively. The Young’s modulus did not change significantly either, from 76.5 GPa at room temperature to 73.1 GPa at 1000°C. The strain to failure was 0.30% at room temperature and 0.27% at 1000°C. After heat-treatment at 1000°C for 100 hours, the retained room temperature strength was 187 MPa and the strength at 1000°C was 176 MPa. The corresponding Young’s modulus values were 82.1 GPa and 78.6 GPa. The strain to failure was approximately 0.28% in both cases. The strength after 150MPa creep loading for 100 hours at 1000°C was 209 MPa, which indicates some form of strain hardening. John et al. reported a strength after 100 hours of creep at 1100°C of 145 MPa, corresponding to 80% of UTS. (Creep load not mentioned).

John et al. have reported that Nextel 720/AS is notch -insensitive at temperatures below 1000°C but that the behaviour exhibit some notch sensitivity at temperatures above 1100°C. Tests were performed on double-edge notched specimens. The notch-sensitivity increased significantly after creep loading at 1100°C. However, the results are evaluated on the basis of the initial stress concentration factor, Kᵥnet, and it can be questioned if that relationship can be applied here, since Kᵥnet is valid only for purely elastic material.

As these materials are intended for long term use at elevated temperature, the long-term thermal durability is an important factor. Jurf and Butner observed a decrease to about 70%
untreated strength at room temperature after 1000 hours at 1100°C. It was suggested that the primary explanation for the loss in strength is matrix densification rather than degradation of fibre strength. A severe 70% decrease in strength was observed after 1000 hours at 1100°C for a Nextel 720/AS which contrasted with Nextel 720/mullite-alumina composite where no loss in fracture strength was detectable after 1000 hour exposure at both 1100 and 1200°C. This supports the suggestion that it is the matrix rather than the fibre that suffers degradation. Long-term ageing has also been performed by Siemens-Westinghouse. At 1100°C the unnotched strength after 100 hours was reduced by over 25% and after 2600 hours by over 55%. A heat-treatment of 3000 hours at 1000°C led to a decrease in strength of about 23%. The suggested explanation of the degradation is embrittlement due to densification of the matrix and possibly a phase change.
4 EXPERIMENTAL

Regardless of how a ceramic green-body is produced, there will almost always be a step in the production where the ceramic powder is immersed in a liquid, for example to improve the milling of the powder, to help break down agglomerates, to mix the powder with sintering aids or to mix different materials. For advanced structural ceramics the particle size is generally sub-micron in which case colloidal forces become more important than gravity in liquid suspensions. Sections 4.1 and 4.2 give details not published elsewhere about two different methods of producing all-oxides composites taking into account such effects. Sections 4.3-4.5 introduce experiments described further in appended papers. Section 4.6 describes measurement of the fracture characteristics of Saphikon fibres on the basis of Weibull statistics.

4.1 Dip Coating

4.1.1 Background

Composites were produced by coating each fibre individually with the matrix in the form of a slip of polycrystalline alumina powder. Consolidation was performed by pressureless sintering. This method produces composites with an ideal uniform fibre spacing, where the fibre volume fraction can be easily varied by changing the thickness of the coated layer. Pressureless sintering also permits a greater choice of shape than is possible with hot pressing. The pressureless sintered composites can if desired be further densified in a post-sinter, hot isostatic pressing process.

A slip can be either water-based or based on organic solvents. Water is for obvious reasons a more convenient solvent to handle. No health or environmental precautions need to be taken and it is a cheap solvent, with no risk of explosion. However, in order to decrease the evaporation time organic solvents are often used. The risk of cracking during drying is also less with an organic solvent due to their low surface tension. Moreover a non-polar solvent gives low ionic solubility and no dissociation. It is possible to create repulsive forces between particles, for example to avoid agglomeration, by adsorbing surfactants or polymers on the surface of the powder. Acetone is a low-polar solvent but is difficult to use in an alumina slurry. Instead two common solvents are MEK/ethanol (methylethylketone) and TRI/ethanol (trichlorethylene).

The first step in a slip preparation is to mix and deagglomerate the powder in the solvent (water or organic solvent). Soft agglomerates (due to van der Waals forces) are easily broken up into primary particles; stirring is often sufficient. Hard agglomerates (due to chemical bonding) need higher forces, and milling is often used. In order to stabilise the primary particles so they do not again form clusters a dispersing agent is used to create appropriate repulsive forces between the particles. The dispersing agent must be added first to avoid competitive adsorption. In Figure 4.1 different principles used for stabilising colloidal particles in a liquid are shown.
Experimental

Fig. 4.1. Methods of stabilising colloidal ceramic particles in liquids.  

The simplest dispersing strategy in a water-based system is to change the pH, but this can lead to corrosion of the slip container and the raw material. It is also difficult to keep the pH stable, it will change when the powder is immersed in the water. Another problem with the use of pH as a way to achieve electrostatic stabilisation is that many oxides have an increased solubility at the very high or very low pH-values, that are often needed to achieve stabilisation. However, even if the pH value is not used for dispersing it is important to control the pH value because H⁺ and OH⁻ ions can react with the surface hydroxyls of the oxide. An oxide immersed in water always has hydroxyls on the surface. If the attraction is too strong between the particles they will agglomerate and if on the other hand the repulsion is too strong it will lead to low packing density.

The isoelectric point (iep) is the point at which the electrophoretic mobility of the particle is zero. Suspensions show colloidal instability in the region of the pH_{iep}, where the rate of coagulation has a maximum value. The system is more stable on either side of the pH_{iep}. Stability can be easily obtained in a slip consisting of oxide powder in water by adjusting the pH. The isoelectric points for Al₂O₃ and ZrO₂ are 9 and 7 respectively.

A binder is used to render the coated layer more flexible and minimise the risk of cracking. Latex binders are one of the most common binders. Latex is a dispersion of a polymer in an aqueous medium.

4.1.2 Materials

The fibres used were single crystal aluminium oxide fibres (Saphikon Inc.) oriented in the c-axis direction. Their properties as quoted by the supplier were: density 3.97 g/cm³, tensile strength 2100-3400 MPa at room temperature and Youngs modulus 414 GPa. The average diameter of the fibres was 135 micrometer.

The slip used for dip-coating of the fibres and also slip-casting of bundles of fibre/tube pairs in the tube-cladding method (described in section 4.2 and Paper I) was an aqueous suspension of powder from Alcoa Chemicals, Alcoa A16SG, which is an alpha-alumina powder with an average grain size of 0.6 microns. The dispersing agent was Dispex 40 (an ammoniumpolyacrylate), which is an electrosterical dispersant. The binder was a latex from Mowolith DM 765, with a Tg of -16°C and a solid content of 50 wt% in aqueous suspension. It is a surfactant with one hydrophilic end (attracted to H₂O) and one hydrophobic. It becomes insoluble in water after drying which is an advantage when several layers are coated on top of each other. It produces a rather soft layer.
Experimental

The solid content of the slip was 55 vol% powder. It is desirable to have as high solid content as possible to minimise the risk of cracking after drying and to achieve a high viscosity of the slip so that it will not run off the fibres. However, viscosity increases with solid content as indicated schematically Figure 4.2. Within a narrow composition range there is a marked increase in viscosity, making the slip very difficult to reproduce, since a slight change in powder content will give a very large change in viscosity. Thus it is necessary to have a powder content below the critical range.

55 vol% solid content was found to be the limit for this slip system after preliminary tests with a 60 vol% slip exhibited large variability in viscosity. Nevertheless, it is an advantage to increase the viscosity of the slip with the help of solid content so that a thickener is not needed. The composition of the slip finally employed is given in Table 4.1.

![Viscosity versus solid content](image)

**Fig. 4.2.** Viscosity versus solid content.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Density [g/cm³]</th>
<th>Weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td></td>
<td>102.8</td>
<td></td>
</tr>
<tr>
<td>Dispersing agent</td>
<td>Dispex A40</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Alxoa A16SG</td>
<td>3.98</td>
<td>500</td>
</tr>
<tr>
<td>Binder</td>
<td>Latex DM 765</td>
<td>1.0</td>
<td>64.55</td>
</tr>
</tbody>
</table>

4.1.3 Method and Results

Initially trials were made of slip preparation using only pH-stabilisation, but the result was a very unstable slip. Dispex A40 gave satisfactory results. It buffers at pH 9, so there is no need to measure the pH-value. It was quite soon understood that a binder was necessary to obtain a crack free layer after drying. The first trials involved methylcellulose but this proved to be a very difficult binder to handle. It gives a very viscous and unpredictable slip. Secondary trials were made with PVA 15000 (polyvinylalcohol), a polymeric binder. PVA has long molecule chains that spread in the slip, giving only a small increase in viscosity. The drawback with PVA is that it is water-soluble, so repeated dippings were not possible since previous layers dissolved and the thickness could not be increased. The latex binder, Mowolith DM 765 described above, gave the best results. The latex increases the viscosity of the slip minimally. Its particles are dispersed between the alumina particles in the slip and it is not activated until after drying. (The binding function is not required in the slip itself).
Alumina powder was dispersed in distilled water and Dispex A40 by ball milling for 12 hours. After sieving the binder was added and the slip was mixed for another hour with alumina milling bodies. Initial tests were made in which the surface properties of the fibres were changed by dipping in concentrated HCl before coating. The aim was to improve bonding between the coated layer and the fibre. However, the acid affected the surface of the fibres in an undesirable way (they were partly dissolved); after the change to latex binder, surface modification of the fibre was found to be unnecessary.

The best results were achieved by pulling the fibres out of the slip at a constant speed. In preliminary experiments an equipment was used in which slip was pumped out of the container via a Watson-Marlow pump which pumps by squeezing a tube such that the tube size and the height of the container above the pump determine the speed of pumping (see Figure 4.3). This however, gave an uneven layer because the pumping affected the viscosity of the slip. The maximum speed achieved with two 3.2 mm thick tubes was 2.2 mm/sec which was too slow to achieve a desirable thickness of the coated layer. A schematic picture of the preliminary experimental set-up is given in Figure 4.3.

Rheology measurements carried out in a StressTech, (Rheologica instruments AB), showed the performance of the slip (see Figure 4.4). The large variation in viscosity of the slip at higher particle volume is clearly seen. Normally the viscosity of the slip increases quickly during the first minutes after the stirring is stopped and then reaches an equilibrium. Therefore the slip was stirred ultrasonically before each coating and left for two minutes before coating. An electrical DC motor was used to pull the fibres (the experimental set-up is shown in Figure 4.5) at a uniform speed of 2 mm/min giving a coating thickness of 20 micrometer in the first step. After coating and drying a density of about 55% of theoretical density was achieved.
Fig. 4.4. Rheological measurements of the slip as a function of time after stirring ceases, 
a) solid content 55 vol% and b) 60 vol%.

The speed at which the fibres were pulled out of the slip strongly affected the thickness of
the coating obtained, the thickness being inversely dependent on the pulling rate. Decreasing
rate of pulling permitted an increasing amount of coating to run back off the fibre. In Figure
4.6 the coating speed versus the coating thickness is given. A strictly linear relationship was not
found but some of the data points are based on only a few samples.

Fig. 4.5. Final experimental set-up.
Experimental

![Graph showing coating thickness versus speed](image)

**Fig. 4.6.** Coating thickness versus the speed at which the fibres were pulled out of the slip.

For the coating operation the fibres were cut into appropriate lengths (50 mm) and cleaned in acetone in an ultrasonic bath. They were mounted on the edge of a small plate by means of double-sided adhesive tape. In this way they could be coated ten at a time. The plate was pulled via a pulley using a DC motor. After drying, the end pieces of the fibres where cut off and the fibres where mounted in bundles, held together by a plug of slip material at each end. Then the coated bundles were slip cast in a cylindrical die. The slip-cast layer improved the handleability of the composite as well as providing a protective barrier against reaction with a glass container used in possible HIP processes. Some trials were also made to produce the protective layer by cold isostatic pressing of powder around the sample instead of slip-casting. However, the symmetry of the bundle of coated fibres was destroyed by the high pressures needed to consolidate the powder. Another series of trials was performed to consolidate the bundle of coated fibres prior to sintering by CIP'ing the fibre bundle alone. The intention was to press the flexible layer of the fibres together in order to make them easy to handle and also to decrease the diffusion distances during sintering. Pressures of up to 200 MPa were used but the coated fibres remained separated.

The composites (with a coating thickness of about 100 microns) were presintered in an air furnace, heating at 1 degree per minute up to 500°C and then 5 degrees per minute up to 1000°C. They were then cooled without dwell-time. Pressureless sintering was performed in a conventional, electrically-heated, high temperature furnace in air, by slow heating up to 1500°C and 1550°C respectively, and sintering for one hour. After sintering at 1500°C, the dip-coated layer had a hardness of 1098 HV while the slip cast layer around the bundle had a hardness of 1862 HV. When the temperature was increased to 1550°C, the densification of the matrix increased. Then the hardness of the dip coated layer was 1758 HV and that of the slip cast layer was 2125 HV. The reason for the difference in density between the slip cast layer and the coating (suggested by the hardness difference) is most probably that the slip around the bundle contained no binder, leading to a higher packing density of the alumina powder particles in that layer and consequently a higher density after sintering. In places there was a gap between the fibre and the matrix. This, together with the fairly low density of the slip cast layer suggests that the sintering time- and or temperature should be increased.

The density of the matrix after sintering at the higher temperature was estimated to be around 90%TD. Matrix porosity was also observed metallographically. The locally occurring gaps between the fibre and the matrix, indicated that the matrix had shrunk, but not sintered.
Experimental

around all of the fibres. In no case was there any fibre growth. The composite microstructure is shown in Figure 4.7.

![Image of composite microstructure](image)

Fig. 4.7. Composite after pressureless sintering.

Consolidation by hot isostatic pressing was also performed in the same HIP cycle as in the tube cladding method described in section 4.2 and Paper I, namely at 1500°C and 200 MPa. This achieved practically full density of the matrix. A back-scattered electron-diffraction examination in SEM indicated a microcrystalline structure.

4.1.4 Discussion and Conclusions

The method of preparation and pressureless sintering conditions used resulted in a porous matrix. However for certain applications, porous matrix composites have attractive properties (see section 2.2.3). Since in general the fibre/matrix interface is sufficiently weak to provide crack deflection behaviour without the need of an interfacial layer. Even so, there exists a potential for increased matrix density through increased sintering temperature. Moreover, the density achieved is probably sufficient to permit encapsulation-free hot isostatic pressing.

The method described above seems to be a possible way to produce composites. The volume fraction fibres could be varied with the thickness of the coated layer by varying the speed with which the fibres are pulled out of the slip. Coated layers between 5-45 microns were produced corresponding to volume fractions of 1 to 36% of fully dense matrix. The coated layer was quite uniform and smooth. For a given pulling rate the coating thickness varied within ± 15%. Adequate contact between the fibre and the matrix was achieved at most places. At some locations a gap was observed between the fibre and the matrix suggesting that the sintering temperature and/or dwell time should be increased.

4.2 Tube Cladding

A novel technique, originally proposed for producing metal matrix composites has been tested on an all-oxide composite, consisting of sapphire fibres in an alumina matrix. It involves cladding of individual large diameter fibres with the matrix material in the form of pre-sintered alumina tubes with appropriate diameter. Consolidation is carried out using hot isostatic pressing (HIP). The method is described in detail in Paper I.
4.3 Notch Sensitivity

The tensile response and notch-sensitivity of a commercially available Nextel 720/AS matrix composite were studied at ambient and elevated temperatures as well as after heat-treatment. The specimens were straight-sided with a centre-hole notch, drilled with a carbide drill. Further description of the material testing details and results are given in Paper III and V.

4.4 XRD and Raman Spectroscopy

X-ray diffraction is an elegant way to study different phases in a material. It has been used on fibres (see Paper II) and on composites (see Paper III and V).

Raman spectroscopy makes it possible to focus on a spot of the material and not as in the case of XRD on an area of the material. Raman spectroscopy resembles infrared adsorption, but an important advantage of Raman spectra over infrared is that water does not cause interference, which means that Raman spectra can be obtained from aqueous solutions. The sample is irradiated with a laser source of visible or near-infrared monochromatic radiation. The spectrum of the scattered radiation is measured at some angle (often 90°) with a suitable spectrometer. The wavenumber shift is the difference in wavenumbers (cm\(^{-1}\)) between observed radiation (scattered by the molecules) and that of the source. Raman shifts are independent of the wavelength of excitation, i.e. it does not depend on the laser source used.\(^1\)\(^2\) Raman spectra were obtained on fibres and matrix in a commercially available composite before and after heat-treatment. The results are presented in Paper V.

4.5 Infra-Red Camera

During loading and failure of a material damage mechanisms and defects can lead to local temperature variations in the material which can be detected by an infra-red camera.\(^3\) This technique was used to monitor the failure processes during the tensile testing of notched Nextel 720/AS composites. The experimental method and results are described in Paper IV.

4.6 Tensile Testing of Fibres

It is well known that ceramic fibres exhibit a scatter in fracture strength as is characteristic for brittle solids generally. The strength depends on the stress needed to propagate an existing crack or flaw in the fibre. A statistical method generally accepted to describe the fracture strength of brittle materials is that proposed by Weibull.\(^4\)\(^5\) This approach has been applied to the sapphire fibres used in the composites of this work.

4.6.1 Experimental

Single crystal aluminium oxide (sapphire) fibres from Saphikon Inc. with 3 different gauge lengths (50, 70 and 90 mm) were tested in a miniature material tester (Minimat), with a load cell of 200 N. The gauge lengths were limited to a maximum of 90 mm by the maximum stroke of the Minimat. The fibres were loaded at room temperature in tension with a speed of 0.5 mm/min, until fibre fracture. Load and displacement were recorded during testing. For gripping, each end of the fibre was mounted between polymer tabs (GF/EP) by gluing. The
adhesive used was a 2-component epoxy, Araldite 2011. The specimen geometry is shown in Figure 4.8.

![Figure 4.8. Geometry of fibre test specimens (L=50, 70, 90 mm)](image)

Brittle fibres are often very sensitive to surface damage and consequently the intrinsic fracture stress distribution of a virgin fibre can be changed significantly by the superposition of a population of strength-determining flaws. These would be expected to reduce the average strength as well as changing the Weibull modulus. In order to investigate the above assumptions and to determine how sensitive Saphikon fibres are to handling, the diameter of one set of fibres was measured with a screw micrometer before the tensile testing in contrast to the usual microscope measurement.

Figure 4.9 shows a typical stress-strain curve obtained from the fibres. The fibres showed near-linear elastic behaviour up to fracture. Initially, however, the curve was not linear; this is most probably due to the fact that the fibres were not perfectly stretched initially and that some sliding in the grips occurred. The small jumps on the curve, marked with arrows are due to slipping in the grips but this did not affect the maximum fracture load recorded. The steepest part of the stress-strain curve was used to determine Young's modulus. Every specimen was investigated after fracture to ensure that fracture did not only occur at the end tabs. In such cases the sample was not included in the results. The stress at fibre fracture is denoted $\sigma_{fr}$ and is given in MPa.

![Figure 4.9. A typical load-displacement curve for the tested Saphikon fibres.](image)

The strength data was treated in terms of the simple three parameter Weibull function:
\[ P_s = \exp \left[ -\frac{L}{L_0} \left( \frac{\sigma}{\sigma_0} \right)^m \right] \]  \[\text{[4.1]}\]

where \( P_s \) is the probability of survival at stress \( \sigma \), \( L \) the gauge length, \( L_0 \) the length normalising parameter, here set at 1 mm, \( \sigma_0 \) the stress normalising parameter and \( m \) the Weibull modulus. This gives

\[ \ln \ln \frac{1}{P_s} = \ln L + m \ln \sigma - m \ln \sigma_0 \]  \[\text{[4.2]}\]

In drawing the Weibull plot from \( \ln \ln 1/P_s \) versus \( \ln \sigma \) data, \( P_s \) was defined as \( (N+i)/(N_T+i) \) where \( N \) is the number of fibres surviving the stress \( \sigma \) and \( N_T \) is the total sample size. In constructing the plot as a straight line through the data points, less weight was given to the points at low stress since for these the value of \( P_s \) is statistically less reliable. The median strength of the sample was obtained at the point on the plot corresponding to \( P_s=0.5 \), i.e. \( \ln \ln (1/P_s) = -0.367 \).

### 4.6.2 Results

The Weibull plot for samples of fibres with \( L=50 \) mm is given in Figure 4.10. This shows clearly the effect of introducing surface defects. Fracture median strength is decreased from 2620 MPa to 2057 MPa and \( m \) is increased from 6.1 to 11.5.

**Fig. 4.10.** Showing the effect of mechanical surface damage on the fracture stress distribution of Saphikon fibres.

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Figure 4.11 shows the Weibull plots for the three different fibre lengths. It is seen that as predicted the median strength decreases with increasing length of the tested fibre. The $m$ values derived from the curves were 6.1, 6.7 and 5.5 for the lengths 50, 70 and 90 mm respectively. For a sufficiently large population the $m$ value should not differ but this is an acceptable variation.

The Weibull equation predicts an inverse relationship between median strength and fibre length i.e. a plot of $\ln \sigma_{\text{median}}$ versus $\ln L$ should be linear with a slope of $-1/m$. The three results of this study are shown in such a plot in Figure 4.12. Allowing for the limited data, the result of the tests are roughly consistent with the prediction.

![Graph showing Weibull plots for different fibre lengths.](image)

**Fig. 4.11.** Weibull plots for the three different lengths.

![Graph showing dependence of median strength on fibre length for $m=6$ and $\sigma_0 = 4700$ MPa.](image)

**Fig. 4.12.** Dependence of median strength on fibre length for $m=6$ and $\sigma_0 = 4700$ MPa.

To obtain a reliable value of Young's modulus of the fibres, i.e. avoiding effects of unwanted extension in the grips etc, $1/E_{\text{eff}}$ can be plotted against $1/L$. This should give a straight line which when extrapolated to $1/L=0$ gives $1/E_{\infty}$ since the relative error decreases with increasing gauge length and can be neglected as $L$ approaches infinity, i.e. when $1/L \rightarrow \infty$. Further details on this procedure are discussed in the experimental section of the paper.
0. Such a plot is shown in Figure 4.13. The E-modulus shows a linear dependence on fibre length as expected and is after extrapolation to infinite fibre length 475 GPa. This value agrees well with reported measurements on single crystal sapphire.\textsuperscript{153}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.13.jpg}
\caption{Plot of observed apparent mean Young’s modulus as a function of inverse fibre length.}
\end{figure}

The manufacturer, Saphikon Inc. gives a tensile strength of 3600 MPa for a 25.4 mm fibre measured at a test rate of 0.025 mm/min, compared with 0.5 mm/min in this study. In contrast extrapolation of Figure 4.12 gives an estimated median strength for $L=25.4$ mm of 2870 MPa. This difference cannot reasonably be explained by the difference of test rate which might be expected to have the reverse effect. The difference may simply reflect differences in batch variations or differences in experimental set-up.

\section*{4.7 Bend Testing}

Bending is a convenient way to test a ceramic material because the test involves a simple, relatively inexpensive testbar geometry and the problems of gripping a brittle material are circumvented. Two common variants of bend testing are 3-point bending and 4-point bending. The three-point bend test is common because it is very simple but the 4-point bend test samples exhibit a larger area of maximum stress which means that a more representative strength value is obtained. It is important to state the method quoting strength of a brittle material; the strength of a tensile tested bar will be significantly lower than that of a 4-point bar, which in turn is lower than the 3-point strength due to the volume dependence of defect frequency.\textsuperscript{156} Simple beam theory can be applied if the stress-strain behaviour of the material is assumed to be identical in tension and compression and if the beam is bent into an arc of a circle between outer contacts. Furthermore, the frictional effects at the contact points must be assumed negligible. The loaded bar develops a stress distribution which can be resolved into
Experimental tensile and shear components and which depends on the dimensions of the bar and the relative position of the loading points. The maximum tensile stress is located along the bottom surface of the bar and is given by:  

$$\sigma_{t,pt} = \frac{3PL}{4bh^2} \tag{4.3}$$

where $P$ is the applied load, $L$ is the support span length, $b$ is the beam width and $h$ is the thickness. The maximum shear stress is generally located within the bar close to the loading points and is given by:  

$$\tau_{t,pt} = \frac{3P}{4bh} \tag{4.4}$$

Often the deflection at the centre with respect to support points is measured with a strain gauge. The strain can then be calculated from:  

$$\varepsilon = \frac{6wh}{L^2} \tag{4.5}$$

where $w$ is the measured deflection in the point of applied load.

Equations 4.3 to 4.5 show that the maximum tensile and shear stresses increase linearly with load. Failure of the bar will occur either by tensile or shear failure depending on whether the tensile strength or the shear strength of the material is reached first. In Paper VI bend test bars were examined after testing to determine the failure mode and thereby choose the appropriate failure stress.
5 RESULTS AND DISCUSSION

This work has covered a number of aspects of all-oxide composites including the properties of candidate oxide constituents as summarised in Chapter 3. Among the metal oxides with high melting point, aluminium oxide and zirconium dioxide are a pair that are chemically compatible with each other and therefore have been widely studied as constituents in CMCs. Aluminium oxide is very prone to grain growth at elevated temperature and therefore not suitable as constituent in oxide fibres at ultra high temperatures in its polycrystalline form. Single crystal alumina fibres have been studied extensively, but due to their high cost, they are unlikely candidates for future composites. However, due to their properties and lack of grain boundaries they are suitable for model studies of fracture behaviour. Polycrystalline oxide fibres are susceptible to creep because of their fine grain size. However, recent research indicates that some improvements in creep resistance can be achieved with polyphase oxides, by grain-boundary doping and by the development of axially-oriented grain elongation.

The fracture characteristics of monocrystalline alumina fibres were investigated in the present work on the basis of simple 3 parameter Weibull statistics. The sensitivity of the fibres to damage was revealed by the measurement of the fibre diameter with a screw micrometer prior to testing. This caused a significant reduction in average fracture strength but also an increase of the Weibull modulus i.e. a reduced scatter in strength. The same test data was used to determine the Young’s modulus of the fibre yielding a value of 475 GPa.

Thermal expansion is one of the most important properties of oxide constituents in CMCs. It influences dimensional stability and also the thermal shock behaviour which is a key property in ceramic materials. A mismatch in thermal expansion of composite constituents leads to residual stresses, which can cause cracking already after processing. A convenient method to determine thermal expansion is high temperature X-ray diffraction. An advantage of this method is that it yields information on any anisotropy of thermal expansion with respect to crystallographic directions. Such anisotropy can lead to residual stresses even in single phase, polycrystalline materials. The use of this method has been demonstrated in this work on some polycrystal oxides. Agreement with published data on the same oxides was good. Estimates of residual stress levels in selected composites were made on the basis of the thermal expansion values obtained.

Preparation of composite materials is challenging because the fibres are stiff and fully dense which constrains the sintering of the matrix around them. This work has shown two novel ways of synthesising a composite suitable with hot isostatic pressing as consolidation technique. Dip coating has promising high levels of green density and pressureless sintered density which makes it possible to densify the composite fully by encapsulation-free hot isostatic pressing. This will reduce the cost of production by HIP and also eliminate reaction between the encapsulation material and the oxide. In the case of aluminium oxide and glass encapsulation this is very important since they readily react to form mullite. Dip coating is a method which permits convenient variation of the fibre fraction, simply by varying the speed with which the fibres are pulled out of the slip. Coating thicknesses between 1 and 45 microns were produced.

Tube cladding is a technique which has been used successfully for metal matrix composites and in this work it has been shown to be applicable to an all-oxide composite. The method involves cladding individual large diameter fibres with the matrix material in the form of pre-sintered alumina tubes with appropriate diameter. The use of matrix tubes pre-sintered to near full-density implies that very little shrinkage is necessary in the axial direction of the composite thus avoiding problems associated with shrinkage mismatch between fibre and matrix. An appropriate hot isostatic pressing cycle was derived, which induced full compaction of the spaces between fibres and tubes and between tubes presumably by creep processes. The
Results and Discussion

A hot isostatic pressing cycle was designed so that the matrix was allowed to soften before full pressure was applied, in order to avoid fracture and crushing of the tubes. There were some growth of the fibres at the expense of matrix grains which indicates that the temperature should be decreased slightly.

The second half of the work in this thesis concerned mechanical properties of all-oxide CMCs. An aluminium oxide composite reinforced with zirconia coated single crystal alumina fibres has been thoroughly investigated by push-out testing of fibres, bending and tensile tests of the CMC as well as compression creep in the axial direction. The fracture behaviour was not as pseudo-ductile as desired but non-catastrophic failure of the composite was obtained through extensive fibre pull-out.

The notch-sensitivity of a commercially-available all-oxide woven composite with a porous matrix has been investigated. The material exhibited non-brittle behaviour and moderate notch-sensitivity at room temperature, 1000 and 1100°C. This was due to extensive fibre-matrix debonding and shear damage in the matrix. Material with the fibres oriented ±45° to the loading direction also had low notch-sensitivity. They exhibited a remarkable increase in strength after thermal exposure and when tested at 1000°C. These effects can be attributed to simultaneous sintering and creep of the matrix.

Extended heat-treatment at 1000°C and shorter exposure at 1100°C degraded the material significantly, which for the 0/90 material was seen as a large reduction in strength and strain to failure. A model based on fracture mechanics was applied successfully to describe the behaviour of the 0/90 material. The model involves two parameters, namely an effective fracture toughness and an effective damage zone length. These parameters were constant (i.e. independent of the notch hole diameter to width ratio) for a given thermal exposure but decreased consistently with thermal exposure temperature and time. Thermal exposure to 1100°C led to an almost fully notch sensitive material, with a corresponding decrease in fracture toughness and damage zone length. The causes of the degradation was shown to be a combination of matrix densification and increased fibre/matrix bonding. Some degradation of the fibres may also have occurred. Local formation of cristobalite was detected by X-ray diffraction but was not be believed to have a large effect on the embrittlement of the composite.

The viability of using an infra-red camera to study the progression of damage in a CMC has been demonstrated. The above all-oxide woven composite was subjected to mechanical cyclic loading. Temperature differences due to frictional heat generated between fibre bundles and the matrix could be detected with the camera as well as matrix cracks, which were cooled due to the inflow of air. It was possible to study the formation and propagation of damage bands that initiated the ultimate failure of the composite. In the specimens with ±45° fibre orientation the bundles are stretched and separated without actual failure of the bundles. The fibre bundles are re-aligned during stretching which is demonstrated as a swelling of the composite. Also material with 0/90 fibre orientation showed occasionally fracture paths oriented diagonally from the centre hole, which is an indication of shear damage in the composite.
6 SUMMARY OF APPENDED PAPERS

Paper I
This paper presents a possible method of producing long fibre reinforced ceramic matrix composites. The method involves cladding individual fibres with the matrix material in form of pre-sintered tubes with appropriately small diameter. The composite is then hot isostatically pressed (HIP). A HIP cycle was found that led to full densification of the composite without visual damage to the fibres. The method produces composites with an ideal uniform fibre spacing; samples of cylindrical shape suitable, for example, for uniaxial testing can be produced.

Paper II
A significant factor in the mechanical behaviour of ceramics, both single phase and as composites, is their thermal expansion and crystallographic anisotropy. The toughness and strength of the composite can be influenced by local residual stresses due to the thermal expansion mismatch of different phases. Moreover, the anisotropy of thermal expansion can give local stress variations from grain to grain within an individual polycrystalline phase. In this paper, reported data on the thermal expansion coefficients of oxides having potential as constituents in high temperature composites are reviewed and complemented with additional measurements made using high temperatures X-ray diffraction.

Paper III
The tensile behaviour of a continuous fibre-reinforced porous matrix composite was investigated in the presence of circular centre holes on samples with variable widths and hole/width ratios. The tests were performed at ambient temperatures both before and after thermal exposure as well as at elevated temperatures. Two different fibre architectures were examined, 0/90° and ±45° to the loading direction. It was found that both orientations were only mildly notch sensitive at ambient temperature. The notch sensitivity increased after thermal exposure.

Paper IV
The evolution of damage in a continuous fibre-reinforced porous matrix composite was investigated using an infra-red camera during tensile tests. There were two fibre orientations, 0/90° and ±45° to the loading direction. Temperature differences due to friction between fibre bundles and matrix were manifested as bright regions due to heat dissipation, whereas matrix cracks appear as dark lines due to the inlet of air. It was possible to detect the formation and propagation of damage bands that ultimately lead to failure of the composites. Test specimens with ±45° fibre orientation exhibited necking which was accompanied by the realignment of fibre bundles in the loading direction.

Paper V
The thermal degradation of the same composite as in Paper III and Paper IV was investigated further in this paper. In the 0/90° material the material was embrittled after thermal exposure which resulted in reduced fracture strength, reduced strain to failure but also reduced fracture toughness and damage zone size. The material became more notch-sensitive after thermal exposure. The ±45° composites was also embrittled with reduced strain to failure but an increase in fracture strength. The embrittlement is thought to be mainly due to localised densification of the matrix and an increase in fibre/matrix bonding. The embrittlement of the 0/90
composites could be successfully characterised in terms of an effective fracture toughness and effective damage zone length derived on the basis of a simple linear elastic fracture model.

**Paper VI**
The mechanical properties of an all-oxide composite reinforced with large diameter sapphire fibres with porous interphase between matrix and fibres were investigated. Two fibre orientations were studied, unidirectionally aligned and 0/90° oriented to the loading direction. The study included the stress-strain response in both tension and bending, as well as a characterisation of the interphase by push-out testing and by the pull-out distribution. The material response at elevated temperatures was investigated by creep testing. Values were obtained for the composite tensile strength and shear strength as well as the interfacial friction stress. The stress-strain curves were unlike those normally observed for small diameter fibre composites. Possible explanations for this in terms of micromechanical processes are discussed.
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Synthesising of a Model Composite in the Oxide/Oxide System:
Alumina Fibre Reinforced Alumina Matrix

Advances in Science and Technology 22, Advanced Structural
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Paper I
Synthesising of a model composite in the oxide / oxide system: alumina fibre reinforced alumina matrix.

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Ceramic matrix composites have attracted big interest as potential material for high temperature applications. To avoid one of the main problems, namely oxidation at higher temperatures, interest has increased for systems where both reinforcement and matrix material are ceramic oxides. This work presents a possible method of producing long fibre reinforced ceramic matrix composites. The method was applied to single crystal aluminium oxide fibres in a polycrystalline alumina matrix and involves cladding individual fibres with the matrix material in the form of pre-sintered tubes with appropriately small diameter. The composite is then hot isostatically pressed (HIP), by putting several fibre-tube pairs in a container of required diameter. A HIP cycle was found that led to full densification of the composite without visual damage to the fibres. The method produces composites with an ideal uniform fibre spacing; samples of cylindrical shape suitable, for example, for uniaxial testing can be produced.

1. INTRODUCTION
Oxide/oxide composites have attracted considerable interest due to their ability to withstand oxidation at high temperatures. The material is reinforced with long fibres in order to decrease the brittleness at lower temperatures and to improve creep strength at high temperatures\textsuperscript{1,2}. Long fibre ceramic matrix composites can be manufactured in a number of ways, e.g. chemical vapour infiltration (CVI) or hot pressing of slurry-infiltrated fibre preforms being two common methods. However, there are some drawbacks to these methods. For example, CVI generally requires long processing times while hot pressing methods are very restricted with respect to the shape of component that can be produced. The purpose of the present work was to develop a method based on hot isostatic pressing (HIP) to produce uniaxially reinforced cylindrical specimens suitable for tensile testing.
The method involves producing long fibre reinforced ceramic matrix composites, by cladding individual, large diameter fibres with the matrix material in the form of tubes with appropriate diameter, a method that has been used successfully to produce metal matrix composites. The composite can be consolidated by hot isostatic pressing to produce composites with an ideal uniform fibre spacing.

2. MATERIALS
The fibres used were single crystal aluminium oxide fibres (Saphikon Inc.) oriented in the c-axis direction. Their properties as quoted by the supplier were: density 3.97 g/cm$^3$, tensile strength 2100-3400 MPa at room temperature and Young's modulus 414 GPa. The average diameter of the fibres was 135 micrometer.

The tubes used for the matrix were sintered tubes supplied by Friatec AG, having a relative density of 99.7% and a mean grain size of 10 micrometer. Their inner and outer diameters were 200 microns and 500 microns respectively.

3. METHOD
The fibres and tubes were cut in desired lengths and cleaned in acetone in an ultrasonic bath. One fibre was put into each tube and a bundle of fibre/tube pairs was then covered with a protective layer of alumina by slip-casting partly in order to hold the bundle together during sintering, and partly to avoid reaction with the glass encapsulation material during the HIP cycle. (Hot isostatic pressing). The slip was an aqueous suspension of a powder from Alcoa Chemicals, Alcoa A16SG, which is an alpha-alumina powder with an average grain size of 0.6 microns. The dispersing agent was Dispex 40 which is an electrosterical dispersant. The solid content was 55 vol%. Selected fibres were also coated with the slip before insertion into the tubes in order to see whether this was a feasible method to reduce the free space between fibre and tube.
The composites were presintered in air in a conventional furnace by heating at 1 degree per minute up to 500°C and then 5 degrees per minute up to 1000°C. They were then cooled without dwell-time. The samples were encapsulated for HIP in Vycor glass tubes under vacuum at 700°C. The composites were HIPed at 1550°C and 200 MPa pressure in an ABB model QIH/9 press using argon as pressing medium. On the basis of a number of preliminary HIP trials, the following HIP cycle was chosen:

1. Heating without applied pressure to 1200°C at 20°C/min followed by 30 min dwelltime to stabilise the temperature.
2. Heating from 1200°C to 1550°C at 20°C/min with simultaneous increase in pressure to about 35MPa.
3. While holding at 1550°C, the pressure was increased to 68 MPa and then held at that pressure for 1 h before being raised to 200MPa over a period of 1.5 h. At this point the temperature had been maintained at 1550°C for a total of 3h.
4. Continued hold at 1550°C and 200MPa for 80 min.
5. Cooling at 15°C/min to 1100°C and then 6.7°C/min to room temperature with corresponding fall in pressure.

HIPed specimens were mounted in epoxy resin and ground and polished for metallographic examination. They were examined in an Olympus optical microscope and a CAMSCAN scanning electron microscope. It was not possible to detect elements with atomic number less than 10 using this instrument.

4. RESULTS
The tubes had shrunk around the fibre in the desired way, see figure 1. The mechanism involved must have been creep since the tubes were almost fully dense from the start. No triple point cavities between the tubes were observed, which indicates that the composites were fully densified. The fibres largely preserved their shape and size,
Sapphire fibre exhibiting growth (the fibre diameter is 148 μm measurably larger than the original fibre diameter). (Optical micrograph).

but in some places a tendency for fibre growth was observed indicating that this is probably the highest time/temperature combination possible for this method.

The state of the interface between fibres and tubes was in general satisfactory but at some places glass from the encapsulation cylinders appeared to have infiltrated the matrix grain boundaries in zones close to the fibre/matrix interface. (Figure 2). This was confirmed by the presence of relatively high contents of silicon in the phase between the grains. The encapsulation glass has a relatively low viscosity at the HIP temperature and an effective barrier is necessary to prevent infiltration into the large channels initially present between fibre and matrix tubes. In the present case, it is presumed that the slip-cast coating must have cracked locally during the processing. Following infiltration the silica is expected to react with the alumina to form mullite or an alumina-silica glass phase and thereby infiltrate the matrix grain boundaries.

As indicated above, selected fibres had been coated with slip prior to insertion into the matrix tubes. It was found that the slip coating appeared not only to have densified but also to have become monocrystalline and coherent with the fibre. (Figure 3).
FIGURE 2
Fibre/matrix interface region showing infiltration of matrix by encapsulation glass (SEM image).

FIGURE 3
A fibre in the HIPed composite that had been pre-coated with alumina slip prior to insertion in matrix tube. Diam. including coating 210-230 μm. (optical micrograph).
5. DISCUSSION AND CONCLUSIONS
The method described shows some promise as a method to produce uniaxial, long-fibre reinforced oxide/oxide composites with large diameter fibres. The use of matrix tubes presintered to near full-density implies that very little shrinkage is necessary in axial direction of the composite thus avoiding problems associated with shrinkage mismatch between fibre and matrix. The present study demonstrates that -using an appropriate HIP cycle- full compaction of the spaces between fibres and tubes and between tubes by a creep process is possible. The HIP cycle chosen was designed to permit softening of the matrix before full pressure was applied in order to avoid fracture and crushing of the tubes. Although little visible damage to the fibres was observed some growth of the fibres at the expense of matrix grains indicates that the HIP temperature chosen was at an upper allowable limit.

Encapsulation of the composite with a slip cast alumina was not fully effective in preventing infiltration of the outer glass encapsulation presumably due to local cracking. However, this technique could well be effective if optimised and if alternative encapsulation oxides are selected. The method is also amenable to the use of thin coatings on the fibre. In future work interlayers of other oxides will be applied in order to optimise the interfacial properties.

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Thermal Expansion Behaviour of High Melting Point Oxides

Thermal Expansion Behaviour of High Melting Point Oxides

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Abstract

The thermal expansion characteristics of the reinforcement and matrix constituents in ceramic composites have a strong influence on a number of aspects of the composite performance. Thus the toughness and strength of the composite can be influenced by local residual stresses due to the thermal expansion mismatch of different phases. Moreover, in individual polycrystalline phases, local stress variations from grain to grain, generated as a result of anisotropy of thermal expansion in combination with anisotropy of elasticity can influence strength and toughness in similar ways. In the present study, reported data on the thermal expansion coefficients of oxides having potential as constituents in high temperature composites are reviewed and complemented with additional measurements made using high temperature X-ray diffraction.

I. Introduction

The residual stresses existing in polyphase composites as a result of mismatch in the thermal expansions of the constituent phases are known to have a significant influence on the properties of the composites. For example, in metal matrix composites thermal mismatch can lead to plastic deformation, fibre debonding and thermal cycling fatigue failure\(^1\). In ceramic matrix composites the stresses can be sufficient to cause spontaneous cracking in one of the constituents during cooling from elevated temperature. The residual stresses may also be beneficial, leading to an effective toughening of the composite by processes such as enhanced bridging, microcracking and crack deflection\(^2\). Significant residual stresses can also exist in single phase, polycrystalline materials as a result of anisotropy of the thermal expansion. Although the mean stress in a given grain is generally quite low, local stress levels, e.g. at grain triple points, can be high and even determine the strength of the material in the absence of other defects\(^3,4\). However, once again the effect can be beneficial leading to enhanced toughness in certain circumstances\(^5\).

With the above considerations in mind, the purpose of the present work was to present relevant thermal expansion and elasticity data for a number of oxides that have potential as the reinforcement and/or matrix constituents in high-temperature ceramic matrix composites. Existing literature data has been complemented by our own experimental measurements of thermal expansion by means of high-temperature X-ray diffractometry.

A general approximate expression for the mean residual stress generated elastically along a given direction in a given constituent in the microstructure is:

\[ \sigma_i = (\alpha_i - \alpha^r)E^rV^m\Delta T \]  

where \(\alpha_i\) is the mean thermal expansion coefficient of the constituent in the given direction over the temperature range \(\Delta T\), \(\alpha^r\) is the mean coefficient of expansion of the surrounding material over the same temperature range, \(E^r\) is an effective elastic constant dependent on the morphology of the constituent, \(V^m\) a constant dependent on the volume fraction of the constituent and \(\Delta T\) is the temperature change from a stress-free temperature to the temperature of measurement (here it is assumed that \(\Delta T\) is positive for a falling temperature). For the purposes of illustration, two special cases are considered here, namely, (i) the axial stress in the fibres in a two-phase, continuous, uniaxial fibre composite and (ii) the mean stress in a grain in a polycrystalline, single phase material measured in the crystallographic direction exhibiting the maximum tensile stress. In both cases the material is assumed to be cooled down from a stress free state. The stresses are given in the two cases by equations 2 and 3 respectively:

\[ \sigma_f = (\alpha_f - \alpha_m)E_fE_mV_m\Delta T/(V_fE_f + V_mE_m) \]  

\[ \sigma_g = (\alpha_g - \alpha_m)E_gE_mV_m\Delta T/(V_gE_g + V_mE_m) \]
where the subscripts f and m here refer to the fibre and matrix respectively, E is the Young's modulus and V the volume fraction and

$$\sigma_g = (\alpha_g - \alpha_p)G'\Delta T$$

(3)

where g represents a grain measured in the crystallographic direction of highest expansion coefficient, \(\alpha_p\) is the average expansion coefficient of the polycrystalline aggregate defined by \(\alpha_p = (\alpha_a + \alpha_b + \alpha_c)/3\) where the a, b and c coefficients are measured in three mutually perpendicular directions, usually the three principal directions of the crystal lattice, and \(G'\) is an effective elastic modulus corresponding to the average constraint of the aggregate surrounding the grain and given by:

$$G' = G(9K + 8G)/(3K + 4G)$$

(4)

where \(G\) is the shear modulus and \(K\) the bulk modulus [5]. The volume fraction term in this case is unity since only a single isolated grain is considered, all other grains being incorporated in the surrounding matrix. It can be noted that to a good approximation \(G' \approx E/5\).

II. Experimental

With the exception of alumina the oxides chosen for study (listed in Table II) were obtained in powder form with 99.9% purity and particle sizes of 0.2 to 0.5 μm. The alumina was of high purity but in the form of dense sintered material with a grain size of approximately 5 μm. Its thermal expansion behaviour was measured both in the bulk and crushed powder state. The fine particle size of the other oxides led to significant line broadening and they were therefore heated at 1450°C for 1 h in order to coarsen their grain size and then crushed.

The thermal expansions of the oxides were measured in air between room temperature and 1200°C in a Philips X'Pert MPD powder X-ray diffractometer with a PW 3050/20 goniometer in a Buhler HDK 2.4 high temperature chamber using a Pt heating element. Diffraction scans were made at 200°C intervals starting at 200°C; thus the expansion coefficient was measured as average values between room temperature and these levels. The heating rate was 5°C/min with a 10 min hold before each scan. The temperature was measured with a Pt-13%Rh/Pt thermocouple welded to the platinum sample holder and is estimated to have an accuracy of ±10°C. Diffraction patterns were measured in a 2θ range of 10-80° using Cu Kα radiation. The peaks used for calculation were chosen on the basis of good resolution and the absence of overlapping, neighbouring peaks.

III. Results and Discussion

The elasticity data used here is summarised in Table I in terms of Young's modulus, Poisson ratio and the estimated value of \(G'\). The data is based on data reported in the literature and is wherever possible derived from single crystal constants as a mean of the Hashin-Strikhman bounds for a random aggregate[6]. Where several sources have been available a source deemed to give representative values was selected. Where single crystal data has not been available, the K and G values have been estimate from E and v using the standard relationships between elastic constants.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>E (GPa)</th>
<th>v</th>
<th>G' (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>298</td>
<td>0.18</td>
<td>65</td>
<td>[7]</td>
</tr>
<tr>
<td>HfO₂</td>
<td>250*</td>
<td>0.27</td>
<td>57</td>
<td>[8]</td>
</tr>
<tr>
<td>ThO₂</td>
<td>250</td>
<td>0.28</td>
<td>56</td>
<td>[9]</td>
</tr>
<tr>
<td>ZrO₂ (+3Y₂O₃) tetragonal</td>
<td>205*</td>
<td>(0.25)</td>
<td>42</td>
<td>[8]</td>
</tr>
<tr>
<td>ZrO₂ (+8Y₂O₃) cubic</td>
<td>221</td>
<td>0.31</td>
<td>44</td>
<td>[10]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>405</td>
<td>0.23</td>
<td>84</td>
<td>[11]</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>180*</td>
<td>0.29</td>
<td>36</td>
<td>[8]</td>
</tr>
<tr>
<td>Al₆Si₂O₁₃ (mullite)</td>
<td>145*</td>
<td>(0.25)</td>
<td>30</td>
<td>[12]</td>
</tr>
<tr>
<td>Si₃ZrO₃</td>
<td>(200)</td>
<td>(0.25)</td>
<td>41</td>
<td>-</td>
</tr>
<tr>
<td>Y₃Al₅O₇ (YAG)</td>
<td>283</td>
<td>0.25</td>
<td>58</td>
<td>[13]</td>
</tr>
</tbody>
</table>

*E measured on bulk polycrystal; () indicates arbitrary estimate since no data available.
Values of thermal expansion coefficients are given in Table II together with the residual stresses estimated for the two cases represented by equations 2 and 3. In both cases it was assumed that the material was cooled to room temperature from 1000°C where it was free from stress. In the case of the fibre composite (Equation 2) it was assumed that the matrix is 50 vol% alumina with a thermal expansion of $8.46 \times 10^{-6} \text{K}^{-1}$. Since the fibre content is set at 50 vol% the results presented would be the same for a composite with the fibre and matrix reversed - i.e. alumina fibres in the oxide as matrix with sign of the stress reversed. Similarly, the average axial stress in the matrix is equal to that in the fibre but with opposite sign. From this it follows that many oxide fibres can generate significant axial compressive or tensile stresses in an alumina matrix and vice versa thereby influencing the fracture behaviour of the composite. In certain cases the stresses could be sufficient to lead to local crack formation.

Comparing the thermal expansion results for alumina in the bulk and powder form it can be noted that the coefficients calculated for the polycrystalline aggregate, $\alpha_p$, should be identical. That they differ slightly is a reflection of a small deviation from reproducibility in the measurement. In Table III the results for the bulk sample have been corrected using the powder sample as reference. This reveals that the directed coefficients for the bulk exhibit lower anisotropy than the corresponding coefficients for the powder. This is to be expected since in the dense polycrystal the anisotropic expansion of an individual grain is constrained by the surrounding material. The difference in the $c_a$ coefficients, for example, should correspond to a strain consistent with the stress estimate given by Equation 3. Thus, for a temperature change of 980°C this strain is $980(9.04 - 8.74) \times 10^{-6} = 2.94 \times 10^{-4}$ corresponding to a stress of approximately 120 MPa which is in fair agreement with the value of 83 MPa obtained with Equation 3.

<table>
<thead>
<tr>
<th>Oxide and reference</th>
<th>$\alpha_a \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_b \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_c \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_p \times 10^6(\text{K}^{-1})$</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\sigma_g$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measured in this work</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$(+3Y$_2$O$_3$) (t)</td>
<td>10.10</td>
<td>10.10</td>
<td>11.20</td>
<td>10.47</td>
<td>268</td>
<td>30</td>
</tr>
<tr>
<td>ZrO$_2$(+8Y$_2$O$_3$) (c)</td>
<td>10.90</td>
<td>10.90</td>
<td>10.90</td>
<td>10.90</td>
<td>341</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$ bulk</td>
<td>7.15</td>
<td>7.15</td>
<td>8.15</td>
<td>7.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$ powder</td>
<td>7.53</td>
<td>7.53</td>
<td>9.04</td>
<td>8.03</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>7.34</td>
<td>7.34</td>
<td>7.34</td>
<td>7.34</td>
<td>-137</td>
<td>-</td>
</tr>
<tr>
<td>Al$_6$Si$_2$O$_13$ (mullite)</td>
<td>3.98</td>
<td>6.58</td>
<td>5.56</td>
<td>5.37</td>
<td>-323</td>
<td>36</td>
</tr>
<tr>
<td>SrZrO$_3$</td>
<td>10.10</td>
<td>10.10</td>
<td>10.10</td>
<td>10.10</td>
<td>215</td>
<td>-</td>
</tr>
<tr>
<td>Y$_2$Al$_5$O$_3$ (YAG)</td>
<td>8.15</td>
<td>8.15</td>
<td>8.15</td>
<td>8.15</td>
<td>-50</td>
<td>-</td>
</tr>
<tr>
<td><strong>Literature data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO [14]</td>
<td>14.2</td>
<td>14.2</td>
<td>14.2</td>
<td>14.2</td>
<td>966</td>
<td>-</td>
</tr>
<tr>
<td>HfO$_2$ [14]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.6*</td>
<td>-468</td>
<td>-</td>
</tr>
<tr>
<td>ThO$_2$ [14]</td>
<td>9.4</td>
<td>9.4</td>
<td>9.4</td>
<td>9.4</td>
<td>142</td>
<td>-</td>
</tr>
<tr>
<td>ZrO$_2$(+3Y$_2$O$_3$)(t) [15]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.5</td>
<td>270</td>
<td>-</td>
</tr>
<tr>
<td>ZrO$_2$(+12Y$_2$O$_3$)(c) [15]</td>
<td>9.6</td>
<td>9.6</td>
<td>9.6</td>
<td>9.6</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$ [16]</td>
<td>8.20</td>
<td>8.20</td>
<td>8.98</td>
<td>8.46</td>
<td>-43</td>
<td>-</td>
</tr>
</tbody>
</table>

*Value for 20-1500°C.

<p>| Table III Thermal expansion coefficients of bulk and powder alumina normalised with respect to $\alpha_p$ |
|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>Bulk</th>
<th>$\alpha_a \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_b \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_c \times 10^6(\text{K}^{-1})$</th>
<th>$\alpha_p \times 10^6(\text{K}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>7.68</td>
<td>7.68</td>
<td>8.74</td>
<td>8.03</td>
</tr>
<tr>
<td></td>
<td>7.53</td>
<td>7.53</td>
<td>9.04</td>
<td>8.03</td>
</tr>
</tbody>
</table>

IV. Conclusions

Existing information on the thermal expansion of oxides of potential interest as the constituents of high temperature composites has been collected and complemented with measurements made using high-temperature X-ray diffraction. The
advantage of this method is that it readily yields information on any anisotropy of thermal expansion. Such anisotropy is significant since it can create residual stresses even in single phase, polycrystalline materials. The observed thermal expansions can lead to significant residual stresses in certain composites.

References

Effect of Notches, Specimen Size, and Fiber Orientation on the Monotonic Tensile Behavior of Composites at Ambient and Elevated Temperatures

Ceramic Engineering Science Proceedings (2001)
ABSTRACT
The effect of circular center holes on the monotonic tensile stress-strain behavior and strength of a continuous fiber-reinforced oxide/oxide composite was investigated at ambient and elevated temperatures. The material used in this study consisted of 12 layers of un-coated plain weave fabric of Nextel™ 720, with either 0/90 or ±45° fiber orientation with respect to the loading direction, embedded in an aluminosilicate matrix.

100 and 200-mm long straight-sided specimens with center holes were tested for ratios of hole diameter to width \( (a/w) \) between 0.1 and 0.4, and width values between 3 mm and 25 mm. It was found that as-processed specimens with both fiber architectures were notch insensitive at ambient temperature, but exhibited mild notch sensitivity at elevated temperatures. It was also found that the strength of the material was retained after heat treatments at 1000°C, but that it decreased significantly after exposures at 1100°C for periods of time of 20 and 100 hours. The strength of test specimens with 0/90 fiber orientation was found to decrease with increasing width, but no size effects on strength were observed for specimens with ±45° fiber orientation. These results are discussed in relation to the microstructure of the material and its evolution at elevated temperatures.

INTRODUCTION
The development of continuous fiber-reinforced ceramic composites (CFCCs) has been driven by the expectation of significant environmental and economical benefits if these materials are used in energy-related applications at elevated temperatures. In particular, oxide/oxide CFCCs are attractive because they are inherently stable under oxidizing conditions, which are typical of many energy and industrial processes. Two issues that require special consideration for these applications are: the use of data generated in the laboratory with standardized specimens for the design of components of larger dimensions, and the effect of holes and notches on the mechanical properties of these materials. John et al. [1] have found that the same material as in this study was notch-insensitive at ambient temperatures, but changed behavior into a slight notch-sensitivity at temperatures above 1100°C. Kramb, John and Zawada [2] found a large effect of temperature on notched strength. The tensile behavior of notched samples with ±45° fiber orientation has been investigated by Levi et al. and Heathecote et al. [3 and 4]. Levi et al. found that edge notches could have a strengthening effect on the ±45°samples. The purpose of this study was to investigate the effect of size, holes and fiber orientation on the monotonic tensile behavior of an oxide/oxide CFCC.
MATERIAL
The material used in this study consisted of 12 layers of un-coated plain weave fabric of Nextel™ 720 fibers embedded in a porous aluminosilicate matrix synthesized by slurry infiltration followed by pressureless sintering. The density of the composite was 2.6 g/cm³ and the fiber volume 48%. Test specimens were obtained from rectangular plates 300 mm x 300 mm. Test specimens with 0/90 fiber orientation were obtained from two different plates (A, B) which were processed at different times, while specimens with ±45° orientation were obtained from a single plate (C).

EXPERIMENTAL
Straight-sided tensile bars with length of either 100 or 200 mm and widths between 3 and 25 mm were cut using a diamond wheel. Circular holes were drilled in the center of each bar using a carbide drill. Some of the test specimens were heat-treated in a box furnace at temperatures of 500, 1000 and 1100°C and for periods of time between 20 and 100 hours. Both as-processed and heat-treated test specimens were evaluated in tension either at room or elevated temperature using a servohydraulic mechanical testing machine equipped with hydraulically-actuated grips and a compact furnace with SiC heating elements. The tensile tests were performed at a constant cross-head displacement rate of 10 μm/sec while the deformation of the specimen was measured over a 25 mm gauge section using a strain gauge extensometer at ambient temperatures, and a low-contact force capacitance extensometer at elevated temperatures. The test specimens were studied and examined using light microscopy and X-ray diffraction (XRD) before and after mechanical testing. Post test analysis include fractographic analysis using both light and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION
Stress-Strain Behavior
Representative sets of stress-strain curves are shown in Figure 1 for test specimens with 0/90 and ±45° fiber orientations. The stress-strain curves are non-linear and test specimens with 0/90 fiber orientation were stiffer than those with ±45° fiber orientation. It was found that the strength of the material decreased significantly after heat treatment at 1100°C. Strength values are calculated as

\[ \sigma = \frac{P_{\text{max}}}{t(w-a)} \]  

where \( t \) is the thickness, \( w \) the width, \( a \) the hole diameter and \( P_{\text{max}} \) the maximum tensile load.

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1 Compostie Optics Inc., San Diego CA 99999
2 an electrical Vulcan™ box furnace
3 MTS 810, Eden Prairie, MN
Paper III: Antti et al./ Effect of Notches, Specimen Size, and Fiber Orientation on the Monotonic Tensile Behavior of Composites at Ambient and Elevated Temperatures

Figure 1 a) and b) Representative stress-strain curves of 0/90 samples

Notch sensitivity and size effects

Figure 2a) shows the dependence of strength on $a/w$ for as-processed material with 0/90 orientation. These results indicated that the material is notch-insensitive but also that the strength decreases with increasing width. The notch-insensitive behavior of this material results from the ability of the matrix to crack and redistribute stresses around holes and notches. The decrease in strength with increasing width of the test specimen is the result from the distribution of strengths of the reinforcing fibers and their own dependence of strength on volume. Figure 2b) shows the results for as-processed material with $\pm 45^\circ$ fiber orientation. Although as with specimens with
0/90 fiber orientation these test specimens show notch-insensitive behavior, it was found that there was effectively no loss of strength with increasing width. Because the tensile strength of these materials is controlled by the matrix (unlike the samples with 0/90 fiber orientation that are governed by the fibers) it is likely that the distribution of flaws in the matrix and their size and the size of the specimens are such that there is no direct effect of volume at this scale.

Figure 2 Net section strength for as-received samples as a function of a/w.
Effect of thermal exposure

Heat treatment at 1000°C and above leads to a significant loss in strength for test specimens with 0/90 fiber orientation (Fig 2c). When tested at high temperature, the 0/90 samples exhibited similar behavior to that at room temperature with perhaps a small decrease in strength at 1100°C (Fig 2d). In the ±45° orientation the material was significantly stronger at 1000°C than at room temperature (Fig 2e).

Microstructure

The microstructure of the composite was investigated using light and scanning electron microscopy. It was found that the matrix was densely cracked from the shrinkage that occurs during processing (Fig 3a). Also, matrix-rich regions and large porosity-rich regions were evident inside fiber bundles (Fig 3b). The pores were found to be particularly large in samples with ±45° fiber orientation. Except from these large voids (Fig 3c) the infiltration in the fiber bundles seems to have been successful, see Figure 3d).

The fracture surfaces of the heat treated samples show a brittle appearance, in contrast to the samples tested at room temperature and at high temperature which showed fiber bundle pull-out, see Figure 4a) and b). Scanning electron microscopy of the fracture surfaces revealed the presence of matrix residues on the surface of fibers in as-processed test specimens tested at RT and at high temperature, see figure 4c). However, the fracture surfaces of test specimens that were heat treated at 1100°C had fibers with smoother surfaces, and less evidence of matrix residues. On a few of the samples a possible fracture origin containing fiber-free areas next to the drilled hole was identified, see figure 4d). The fracture behavior and damage mechanisms are discussed further in reference 5.
3a) Shrinkage cracks in fiber-free area inside a fiber bundle. Optical microscope (100x)

3b) Voids inside fiber bundle. (SEM)

3c) Voids in matrix. (SEM)

3d) Showing effective fiber bundle infiltration (SEM)

Figure 3 Representative micrographs of as-received material

4a) As-received 0/90 composite after testing, showing fiber bundle pull-out.

4b) Heat-treated 0/90 after testing, showing brittle fracture behavior.
The X-ray spectrum of as-received, and test specimens that had been heat-treated at 1100°C for 100 hours was obtained between 10 and 90 2Θ at a rate of 1.5 sec/step, in step intervals of 0.03 2Θ. An automatic divergence slit was used with a beam area of 12x16 mm which covered both matrix and fiber regions on the in-plane region of the composite. The matrix in its as-received condition consists of semi-amorphous corundum plus mullite, but after the heat treatment the amorphous phase disappear and its composition changed to corundum, mullite and cristobalite. It was also observed that the (120) and (210) mullite peaks had shifted, which suggests that the silica in the matrix segregates and crystallizes into cristobalite. The relations between the microstructural changes in the matrix and the loss of strength of the composite after heat treatments at temperatures above 1000° are currently under investigation.

CONCLUSIONS

It was found that the as-processed material with both 0/90 and ±45° fiber orientations was notch insensitive at room temperature. The strength of the material was retained after heat treatment up to 1000°C, but it decreased significantly for test specimens with 0/90 fiber orientation after heat treatment at higher temperatures. Test specimens with ±45° fiber orientation were significantly stronger than specimens in the as-received condition tested at ambient temperature after heat treatment and when tested at high temperature. The strength of test specimens with 0/90 fiber orientation was found to decrease with increasing width, but no size effects on strength were observed for specimens with ±45° fiber orientation. XRD results suggest possible crystallization of the silica in the matrix into cristobalite.

ACKNOWLEDGEMENTS

This work was sponsored in part by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Financial support from the Swedish Research Council for Engineering Sciences (TFR) is also acknowledged. The authors thank Professor Richard Warren for helpful discussions and Siemens-Westinghouse and Composite Optics for providing the material used in this study.
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1 R. John, D.J. Buchanan and L.P. Zawada, “Notch-Sensitivity of a Woven Oxide/Oxide Ceramic Matrix Composite”, Submitted for publication, July 1999


Analysis of Damage Evolution in Continuous Fiber-Reinforced Oxide/Oxide Composites under Cyclic Loading, Using Infra-Red Thermography

Ceramic Engineering Science Proceedings (2001)
ANTTI ET AL. // ANALYSIS OF DAMAGE EVOLUTION IN CONTINUOUS FIBER-REINFORCED OXIDE/OXIDE COMPOSITES UNDER CYCLIC LOADING, USING INFRA-RED THERMOGRAPHY

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Oak Ridge National Laboratory
Oak Ridge, TN 37830-6064

Abstract
The evolution of damage in continuous fiber-reinforced oxide/oxide matrix composites was investigated at ambient temperature using an infra-red camera and a servohydraulic testing machine. The material used in this study consisted of 12 layers of un-coated fabric of Nextel™ 720 (either 0/90 or ±45° fiber orientation with respect to the loading direction) and an aluminosilicate matrix. Straight-sided specimens 100 mm long and 12.5 mm wide with center holes were tested for a/w between 0.1 and 0.4. It was possible to record the onset of “necking”, the propagation of cracks in the matrix, and the rotation of fiber bundles during matrix crack growth. These processes were recorded using a fast-speed digital image recorder/analyzer, and the sequence of events is presented.

Introduction
The appropriate design of structures requires a thorough understanding of the effect of flaws from production or holes from design (bolt holes, cooling holes etc) on its mechanical behavior, durability and reliability. The presence of notches and holes lead to a reduction in strength due to the reduction in cross-section area. Further reduction in strength can occur due to stress intensification at the notch tip, unless the material is capable of redistributing stresses around these regions. Several mechanisms capable of reducing stress concentrations in ceramic matrix composites have been identified: the most important include multiple matrix cracking and fiber pull-out.

The objective of this work was to investigate the effect of circular center holes on the tensile behavior of a continuous fiber-reinforced all-oxide composite at room temperature, and to study the evolution of damage in these composites at ambient temperature when subjected to cyclic mechanical loading. This work complements the work reported in reference 1.

Material
The composite consisted of 12 layers of un-coated plain weave fabric of Nextel 720 fibers in a matrix of aluminosilicate with controlled porosity. The composite was fabricated by Composite Optics Inc. using sol-gel techniques followed by pressureless sintering. Fiber volume content is 48%.

Experimental
Straight-sided bars with a length of 100 mm were cut using a diamond saw and circular holes were drilled in the center of each bar using a carbide drill. The samples were cycled at room temperature in tension using an MTS 810 mechanical testing machine. A high-resolution IR camera (Radiance It,
Amber/Raytheon, Goleta, CA) with a 25 mm lens and high-temperature filter was used to map the temperature field during the up-shock test. The IR camera provides both a standard NTSC video output (8-bit resolution) and a 12 bit video interface. Specimens with different hole diameters and widths were tested. Extension and applied load were measured using a 25 mm gauge length extensometer (MTS) and a 25 kN load cell respectively. The specimens were cycled at frequencies between 10 and 30 Hz and stresses between 30 and 170 MPa. Stress-strain data were recorded before the start of the cycling segment and then at regular intervals after a predetermined number of cycles. The damage progression in the specimen was recorded using a fast-speed digital image recorder/analyzer (Image dek II, version 2.1, Amber/Raytheon, Goleta, CA) and a regular video camera.

RESULT AND DISCUSSION

Figures 1 and 2 show a sequence of images obtained with the infra-red camera for test specimens with 0/90 and ±45° fiber orientation, respectively, subjected to cyclic mechanical loading. Bright areas correspond to regions of the test specimen at higher temperatures, which in this case is indicative of heat dissipation due to friction between fiber bundles and the matrix. Dark lines correspond to matrix cracks because of the lower thermal conductivity of air compared to the composites. As can be seen in the sequence of pictures and in the stress-strain curves the damage in the ±45° samples starts earlier in the test than in the 0/90 samples. It is believed that the fracture process starts immediately after initiating loading and progresses during the complete testing sequence. The 0/90 samples are capable of sustaining both a higher net section stress and a larger strain to failure, and it appears like the fracture process is initiated at a much later stage for these specimens.

The 45° bundles start to stretch during loading resulting in the formation of a neck in the region of the hole and the propagation of damage along diagonal lines oriented at 45° with respect to the loading direction. In a later stage the second diagonal starts to break. The width of the damage zones is comparable to the diameter of the hole, as shown in figure 3. Specimens with smaller notches appear to fracture due to unstable and rapid crack growth. However, there is no evidence that the crack initiates at the notch edge, see figure 4b) and figure 6, but rather at an inherent defect in the material. Naturally, this is where the net section stress is the highest. Figure 3 shows pictures of test specimens at the end of the test. The test specimens with ±45° fiber orientation clearly show crack paths that are oriented diagonal to the loading direction, along the fiber bundles. However, also for test specimens with 0/90 fiber orientation containing a small hole cracks can propagate in a direction that is diagonal to the loading direction, see figure 3a). Comparing figure 3a) and b) it can be seen that the crack propagation changes with notch size. In figure 4 the infra-red image of the undamaged test specimen was subtracted from the rest of the pictures, revealing the formation of a deformation band in a very early stage of the mechanical cycling stage.

Stress-strain curves for test specimens with 0/90 and ±45° fiber orientation are shown in figure 5. As a result of mechanical cyclic loading samples with ±45° fiber orientation show significant inelastic straining, while the 0/90 samples mainly exhibit a decrease in stiffness. It was found that test specimens with fibers oriented ±45° with respect to the loading direction exhibited swelling, as seen in figure 3d). This is due to the re-alignment of the fiber bundles with the loading direction.

SUMMARY

This poster presentation demonstrated the viability of using an infra-red camera to monitor the progression of damage in oxide-oxide CFCCs when subjected to mechanical cyclic loading. Friction between fiber bundles and matrix was manifested as bright regions due to heat dissipation, whereas matrix cracks appear as dark lines due to the lower thermal conductivity of air. It was possible to detect the formation and propagation of damage bands that ultimately lead to the failure of the composite.
Test specimens with ±45° fiber orientation exhibited necking and that was accompanied by the realignment of the fiber bundles in the loading direction.

ACKNOWLEDGEMENTS

This work was sponsored in part by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Financial support from the Swedish Research Council for Engineering Sciences (TFR) is also acknowledged. The authors thank Professor Richard Warren for helpful discussions and Siemens-Westinghouse and Composite Optics for providing the material used in this study.

REFERENCES

1M-L. Antti, E. Lara-Curzio; “Effect of Notches, Specimen size, and Fiber Orientation on the Monotonic Tensile Behavior of Composites at Ambient and Elevated Temperatures”; Cocoa Beach Conference, 2001

Figure 1 Damage sequence of a 0/90 composite, width=12.5 mm and hole diameter 5 mm. Loading direction left right.
Figure 2 Damage sequence of a ±45° composite, width 8 mm, hole diameter 0.8 mm

2a) First undamaged picture
2b) Diagonal damage band visible
2c) Necking of the sample, prior to fracture
2d) Increased damage zone
2e) Rotation of fiber bundles
2f) Composite fracture

3a) 0/90 sample with hole diameter 1.2 mm (width 12.5 mm)
3b) 0/90 composite with hole diameter 3 mm (width 12.5 mm), crack path perpendicular to loading direction
3c) ±45° fiber orientation, hole diameter 3.2 mm (width 8 mm)  
3d) ±45° fiber orientation, from side, showing swelling

Figure 3 Micrographs of tested samples showing the crack paths.

4a) Damage zone along fiber bundle visible in an early stage of testing  
4b) Possible fracture origin, dark spot, (see arrow) believed to be a defect.

Figure 4 First undamaged picture subtracted from the pictures in order to enhance the damage propagation. Fiber orientation ±45°.

![Graph](image)

Fig 5a)
Figure 5 Stress-strain curves for cycled composites with 0/90 (a) and ±45° fiber orientation (b).

Figure 6 Micrograph showing severe cracking in matrix-area close to hole. Fiber orientation ±45°. Optical microscope, magnification 10x.
Thermal Degradation of an Oxide Fibre (Nextel 720) / Aluminosilicate Matrix Composite

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Thermal degradation of an oxide fibre (Nextel 720) / aluminosilicate composite

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Abstract
The effect of thermal exposure on the microstructure and tensile stress-strain behaviour has been investigated for composites of woven continuous oxide fibres (Nextel 720) in a porous aluminosilicate matrix. The tensile tests were carried out on straight-sided, centre hole notched plates with 0/90° and ±45° orientations. The as-received material was slightly notch sensitive in that the net section fracture stress decreased somewhat with increasing hole diameter but much less than predicted for an ideally elastic, fully notch-sensitive material. After exposure at 1100°C and for long time at 1000°C the composite was embrittled. In the 0/90 composite this resulted in a reduced fracture strength, a reduced strain to failure as well as a reduced fracture toughness and damage zone size. After exposure for 100h at 1100°C (the most extreme exposure applied) the material also became significantly more notch sensitive and had failure characteristics similar to a monolithic ceramic. The ±45 composite was also embrittled which resulted in a reduced strain to failure but an increase in fracture strength. Density measurements and observations on the microstructure and fracture surfaces indicated that the embrittlement was due mainly to localised densification of the matrix and an increase in fibre/matrix bonding.

Keywords: Composites; Nextel; Notch sensitivity

1. Introduction

It is now well established that continuous fibre reinforced ceramic composites (CFCCs) can be made to have non-brittle fracture behaviour and improved damage tolerance by introduction of a suitably weak fibre/matrix interface. The interphase, if correctly designed, provides a more favourable path for the extension of matrix cracks than penetrating the fibre. The interphase is often coated separately onto the fibres during processing and this involves both an increased production cost as well as an added complexity. It has recently been demonstrated that similar crack-deflecting behaviour can also be achieved by means of a finely distributed porosity in the matrix instead of a separate interphase between matrix and fibres. Delamination has been shown to occur in the matrix and the crack deflects into a plane parallel to the loading direction. In particular oxide/oxide CFCCs exploiting this principle attract interest as candidate materials for use in combustors, exhibiting damage tolerance combined with inherent oxidation resistance. Their anticipated ability to operate at higher temperatures than the superalloys used today is expected to lead to an increased efficiency and a reduced need for cooling air, as well as a decreased emission of NOx gases. The life requirements of the material are high, the aim being several hundred thousand hours at at least 1100°C.

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When designing a structural component, the effect of holes and notches on the mechanical properties is an important practical factor to be taken into consideration. For this reason the mechanical strength of CFCCs has frequently been studied in terms of the notch strength and notch sensitivity. The present work concerns the notch strength behaviour of a commercially available composite consisting of laminated, woven mullite/alumina fibres (Nextel 720) in a porous aluminosilicate (AS) matrix. The results have been presented in general terms in an earlier study. The focus of this study is the thermal instability of the composite microstructure exposed to elevated temperatures and in particular with respect to its influence on notch strength and notch sensitivity. Both 0°/90° and ±45° orientations were investigated.

In common with polymer matrix composites, carbon matrix composites and several non-oxide CFCCs, porous matrix oxide/oxide composites exhibit moderate notch sensitivity. For example, centre hole plate samples with 0/90 orientation at room temperature exhibit a moderate decrease in net section strength with increasing hole diameter. The strength falls towards a limiting value for large hole diameters that generally lies between 60 to 80% of the unnotched strength. The relatively good notch tolerance is associated with the development of an extensive zone of damage developing from the hole with increasing load which effectively reduces the stress intensity at the hole. In dense matrix composites the damage consists of multiple tensile cracking of the matrix combined with fibre/matrix debonding. In porous matrix composites, shear damage of the matrix is thought to make a significant contribution. Their fracture is dominated by shear failure of the matrix. During the composite fracture process the fibre tows can separate without significant fibre fracture. A function of the fibres is to aid the extension of matrix damage thereby reducing the stress intensity. The nature of the centre hole notch test is discussed in more detail in Section 2 below.

Reports on the thermal degradation of porous matrix, all-oxide CFCCs are scarce. Levi et al. report, for an alumina fibre (Nextel 610) reinforced mullite/alumina composite, little change in unnotched tensile behaviour after up to 100h at 1200°C. However, a 2h exposure at 1300°C led to reduced fracture stress and strain to failure. The authors attributed this to fibre degradation rather than to changes in the matrix and suggested that the use of the more stable Nextel 720 fibre should lead to improved thermal stability. Jurf and Butner observed a decrease to about 70% unnotched strength of the 0/90 material studied here after 1000 hours at 1100°C. It was suggested that the primary explanation for the loss in strength is matrix densification rather than degradation of fibre strength. Long-term ageing has also been performed by Siemens-Westinghouse. At 1100°C the unnotched strength after 100h was reduced by over 25% and after 2600 hours by over 55%. A heat-treatment of 3000 hours at 1000°C led to a decrease in strength of about 23%. The suggested explanation of the degradation is embrittlement due to densification of the matrix and possibly a phase change. The present authors are not aware of any earlier reports on the notch strength or notch sensitivity of such composites. However, in a study of edge-notched specimens of a 0/90 Nextel 610/AS composite it was found that the failure mode changed from multiple matrix fracture at room temperature to self-similar crack growth at 950°C. This change led to a significantly increased notch sensitivity.

Nextel 720 fibres consist of a mixture of alumina and mullite grains. The alumina grains have diameters of approximately 0.1μm. These are distributed among larger (0.5μm) mullite grains consisting of many smaller subgrains. Degradation of the fibres has been studied by Deléglise et al.; the authors report that large α-alumina platelets (1.5 microns) formed on the surface after heat-treatments above 1200°C. However, it was found that for 5h exposure the heat-treatment temperature must exceed 1400°C for a significant loss in tensile strength to occur. On the other hand, Petry and Mah found a 9% strength loss after an exposure at 1100°C for 2 hours. Among possible degradation mechanisms they suggest thermal grooving,
grain growth and/or annealing of the mullite subgrain boundaries. Milz et al.\textsuperscript{17} report a severe degradation in fibre strength after heat-treatment at 1300°C (2 hours). They suggest that the strength degradation is due to locally enriched impurities, which in their tests had greater significance since they used a larger gauge length.

2. The notch sensitivity test

As already indicated the main objective of the present study was to investigate the degradation at high temperatures of oxide/oxide, porous matrix composites and in particular through its effect on the notch sensitivity measured in terms of the tensile properties of centre hole panels. This form of notch sensitivity test, though of practical relevance, is somewhat complex in interpretation. In an isotropic, elastically deforming solid, the maximum stress intensification at the edge of a circular notch in an infinitely wide plate loaded in uniaxial tension is a factor of three regardless of hole size.\textsuperscript{18} Thus the strength of an ideally, fully notch sensitive material will be reduced by a factor of three when such a notch is introduced. A fully notch insensitive material will not be weakened since the stress intensification will be dissipated, for example, by plastic deformation. In reality most materials, including long-fibre reinforced composites, exhibit intermediate behaviour leading to a moderate loss of strength that is generally dependent on hole size. The dependence on hole size arises because the circular notch affects and interacts with the material in its immediate vicinity, thereby altering the distribution of the stress intensification; the volume of affected material scales with the hole size.\textsuperscript{18} An added complication in experimental situations is that the stress intensification of a circular hole is affected by the width of the tested plate, decreasing from a factor of three to a factor of two as the ratio of hole size to plate width (a/w) approaches 1,\textsuperscript{19} thus necessitating a finite width correction. It is also to be noted that the stress intensification is altered to some extent by anisotropy of elastic properties.\textsuperscript{20}

A monolithic ceramic might be expected to be close to an ideally notch sensitive material. However, here the measured strength will depend on the interaction of the stress field around the hole with the flaw population in the material thus again introducing a notch size effect. Moreover, for such brittle solids the quantitative assessment of notch sensitivity is somewhat impractical since a unique value of the notch-free strength is difficult to determine due to the stochastic nature of their fracture stress.

A number of semi-empirical models have been proposed to describe the notch sensitivity of long fibre, laminate composites including the effective crack model proposed by Waddoups et al.\textsuperscript{21}, the point stress model\textsuperscript{22} and the average stress model\textsuperscript{22}. Primarily developed for polymer matrix composites they have also proved applicable to long fibre reinforced ceramics. Above all they can be used to predict the effect of hole size on the basis of a limited number of experimental measurements in combination with fitting procedures. More recently, more physically realistic models based on crack bridging mechanisms have been presented which also successfully predict the effects of notch geometry.\textsuperscript{23} However, application of these models requires knowledge of the bridging forces, which usually implies additional experimental measurement.

In the present work the results have been interpreted in terms of the Waddoups approach, not only because of its relative computational convenience but also because it was considered to be appropriate for the composite degraded by heat treatment which was assumed to have become embrittled making measurement of an unnotched strength difficult.
3. Experimental details

3.1. Material

The material in this study consisted of Nextel 720 fibres in a porous aluminosilicate matrix. The plates consisted of 12 layers, with a density of 2.6 g/cm³ and a fibre volume of approximately 48%. The processing of this composite has been presented elsewhere. Test specimens of two different fibre lay-ups (0/90° and ±45°) were produced from rectangular plates of 300x300 mm. Specimens with 0/90 fibre orientation were obtained from two plates (A and B) processed in different batches; ±45° specimens were taken from a third plate (C).

The composites were plain weave with a unit cell of approximately 1200 x 900 microns (Fig. 1). The warp and weft fibre tows had average widths of 250 microns and 340 microns respectively. Furthermore, they exhibited up to 0.5° deviation from the nominal orientation with respect to the side of the test bars in both the 0/90 and ±45° samples.

3.2. Experimental procedure

Tensile tests were performed on centre circular notched straight-sided specimens with a length of 100 mm for tests at ambient temperature and 200 mm for tests at high-temperature. Their width was 12.5 mm. Each tensile bar had a circular centre hole drilled with a carbide drill. The ratio between hole diameter and width of the specimen (a/w) was one of three nominal values (0.1, 0.25 and 0.4). For practical reasons the actual values sometimes deviated somewhat from the nominal.

Specimens were heat-treated in a box furnace at temperatures of 500, 1000 and 1100°C for times between 20 and 3240 hours. The holes were drilled before heat-treatment but dimensions used for stress calculation were measured afterwards. Both as-processed and thermally exposed test specimens were evaluated in tension either at room or elevated temperature using a servohydraulic mechanical testing machine (MTS 810, Eden Prairie, MN, USA) equipped with hydraulically-actuated grips and a compact furnace with SiC heating elements. The tensile tests were performed at a constant cross-head displacement rate of 10 μm/sec while the deformation of the specimen was measured over a 25 mm gauge section using a strain gauge extensometer at ambient temperatures, and a low-contact force capacitance extensometer at elevated temperatures.

The tested specimens were embedded in epoxy and polished and examined in both optical microscope and scanning electron microscope (SEM), both transverse and parallel (LT and TW surfaces) to the loading direction (see the schematic diagram, Fig. 2). The fracture surfaces of both fibre orientations were studied in the SEM, both directly and embedded in epoxy and polished on the LW surface. Density and porosity measurements were performed using the Archimedes method as well as image analysis. The microhardness of the matrix was investigated as a function of heat-treatment time and temperature, using a digital microhardness indenter (Matsuzawa MXT-α) at a load of 100 grams and a loading time of 15 seconds.

Test specimens before and after thermal exposure were investigated with X-ray diffraction (XRD). The X-ray spectra were obtained between 10 and 90° 2θ in step intervals of 0.03 2θ at a rate of 1.5 sec/step. An automatic divergence slit was used with a beam area of 12x16 mm which thus covered both matrix and fibre regions of the composite. High-temperature XRD has also been performed on pure Nextel 720 fibres, in a powder X-ray diffractometer (Philips PW 1710) with a step of 0.03 2θ at a rate of 8 sec/step. After crushing the fibres to a powder heating cycles up to 1400°C were performed with a heating rate of 5°C per minute and a holding time of 10 minutes every 150°C allowing for an additional scan.
Selected samples were also examined using Raman spectroscopy. A Dilor XY 800 triple stage Raman microprobe (JY, Inc, Edison, NJ) and an Innova 308C Argon ion laser (Coherent, Inc., Santa Clara, CA, USA) operating at 514.5 nm with a 300 mW output power were used to record Raman spectra from the fibres and the matrix. The laser was focused onto areas of interest with an optical objective providing a spatial resolution of ~2 μm.

Fig. 1. Fibre fabric structure of the composites.

Fig. 2. Definition of test bar surfaces.

4. Results

4.1. Stress-strain behaviour

Table 1 shows a summary of the tensile strength, stiffness, strain to failure and matrix hardness values of the tested samples in the study. Each set of tensile bars contained a replicate sample to assure reproducibility, which was high. Table 2 shows the results for the ±45° fibre orientation.

Representative sets of stress-strain curves for samples with a width of 12.5 mm and an a/w ratio of 0.25 are shown in Figure 3 (0/90 fibre orientation) and Figure 4 (±45° fibre orientation). It can be seen that the material with 0/90 fibre orientation lost some strength when heat-treated at 1000°C; after 100 hours at 1100°C the strength fell to less than one third of the as-received strength. The 0/90 material lost stiffness when tested at 1100°C, but after heat-treatment the stiffness at room temperature increased. The strain to failure of the samples with 0/90 fibre orientation was severely decreased after heat-treatment indicating embrittlement of the material.

The ±45° material increased in strength after heat-treatment, but the fracture sequences were abrupt and violent compared to the as-received fracture which was a gradual process, indicating an embrittlement after heat-treatment. They also exhibited a significant increase in stiffness after heat-treatment. It is to be noted that with thermal exposure the properties of the 0/90 and ±45 materials approach each other. Most remarkable was the large increase in strength of the ±45 material, with a corresponding increase in strain to failure when tested at 1000°C. This is believed to involve creep mechanisms. Whereas the 0/90 samples fractured by fibre bundle fracture and pull-out (Fig. 5a)), in the samples with ±45° fibre orientation the fracture surfaces could be totally separated with little or no indication of bundle fracture (Fig. 5b)). The fracture is presumably able to occur by matrix failure followed by ply separation.
Table 1. Properties of 0/90 fibre orientation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a/W</th>
<th>Net-section strength [MPa]</th>
<th>Full section stiffness [GPa]</th>
<th>Hardness HV</th>
<th>Strain to failure [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received A (RT)</td>
<td>0.10</td>
<td>201</td>
<td>72</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>203</td>
<td>70</td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>0.39</td>
<td>197</td>
<td>62</td>
<td></td>
<td>0.26</td>
</tr>
<tr>
<td>As-received B (RT)</td>
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<td>204</td>
<td>68</td>
<td>204</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>179</td>
<td>62.5</td>
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<td>0.28</td>
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<tr>
<td></td>
<td>0.42</td>
<td>191</td>
<td>54</td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>200hrs at 500°C (B)</td>
<td>0.10</td>
<td>203*</td>
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<td>0.32</td>
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<tr>
<td></td>
<td>0.29</td>
<td>191</td>
<td>62</td>
<td></td>
<td>0.29</td>
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<tr>
<td>100hrs at 1000°C (B)</td>
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<td>180</td>
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<tr>
<td></td>
<td>0.29</td>
<td>172</td>
<td>66</td>
<td></td>
<td>0.24</td>
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<tr>
<td></td>
<td>0.42</td>
<td>149</td>
<td>57</td>
<td></td>
<td>0.19</td>
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<tr>
<td>3240hrs at 1000°C (B)</td>
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<td>80</td>
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<td></td>
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<td>107</td>
<td>74</td>
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<td></td>
<td>0.42</td>
<td>102</td>
<td>66</td>
<td></td>
<td>0.11</td>
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<tr>
<td>20hrs at 1100°C (A)</td>
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<td>125</td>
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<td>334</td>
<td>0.17</td>
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<tr>
<td></td>
<td>0.25</td>
<td>113</td>
<td>73</td>
<td></td>
<td>0.15</td>
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<td>0.39</td>
<td>114</td>
<td>69</td>
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<td>0.12</td>
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<td>100hrs at 1100°C (A)s</td>
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<td>54.5</td>
<td>90</td>
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<td>39</td>
<td>74</td>
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<td>0.04</td>
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<td>As-rec test at 1000°C (B)</td>
<td>0.09</td>
<td>210</td>
<td>68</td>
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<td>0.35</td>
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<tr>
<td></td>
<td>0.29</td>
<td>171</td>
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<td>0.24</td>
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<td></td>
<td>0.40</td>
<td>186</td>
<td>56</td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>As-rec test at 1100°C (A)</td>
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<td>189</td>
<td>57</td>
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<td>0.35</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>164</td>
<td>63</td>
<td></td>
<td>0.24</td>
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<tr>
<td></td>
<td>0.38</td>
<td>154</td>
<td>53</td>
<td></td>
<td>0.18</td>
</tr>
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</table>

*Failed at grips

Table 2. Properties of ±45° fibre orientation (plate C).

<table>
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<tr>
<th>Sample</th>
<th>a/W</th>
<th>Net-section strength [MPa]</th>
<th>Stiffness [GPa]</th>
<th>Strain to failure [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received (RT)</td>
<td>0.10</td>
<td>64</td>
<td>57</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>61</td>
<td>52</td>
<td>0.19</td>
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<td></td>
<td>0.43</td>
<td>69</td>
<td>47</td>
<td>0.16</td>
</tr>
<tr>
<td>200hrs at 500°C</td>
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<td>61</td>
<td>53</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>64.5</td>
<td>51</td>
<td>0.17</td>
</tr>
<tr>
<td>100hrs at 1000°C</td>
<td>0.09</td>
<td>66.5</td>
<td>56.5</td>
<td>0.24</td>
</tr>
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<td></td>
<td>0.29</td>
<td>66</td>
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<td>0.40</td>
<td>62.5</td>
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<td>0.15</td>
</tr>
<tr>
<td>3240hrs at 1000°C</td>
<td>0.10</td>
<td>91</td>
<td>62</td>
<td>0.27</td>
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<td></td>
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<td>91</td>
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<td>0.16</td>
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<tr>
<td></td>
<td>0.40</td>
<td>96.5</td>
<td>58</td>
<td>0.17</td>
</tr>
<tr>
<td>100hrs at 1100°C</td>
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<td>69</td>
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<td>0.29</td>
<td>93.5</td>
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<td>56</td>
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<tr>
<td>As-rec test at 1000°C</td>
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<td>48</td>
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<td>0.30</td>
<td>81*</td>
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<td></td>
<td>0.40</td>
<td>95</td>
<td>40</td>
<td>0.41</td>
</tr>
</tbody>
</table>

*Failed at grips, because plate C was not perfectly flat which induced bending forces when clamped.
Fig. 3. Representative stress-strain curves of 0/90 samples.

Fig. 4. Representative stress-strain curves of ±45° samples.

Fig. 5. As-received samples after tensile testing, showing extensive fibre bundle pull-out.
The 0/90 stress-strain curves exhibited a relatively distinct fall in slope (knee) situated in the room-temperature tests at a net stress level of between 30 and 50 MPa and a strain of between 0.03 and 0.06 %. This net stress level corresponded to a theoretical intensified stress at the hole of 70-135 MPa. Interestingly, the knee stress and strain was somewhat higher at 1000 and 1100°C (60-90 MPa and 0.07-0.15% respectively). The knee is associated with damage in the composite. Figure 6 shows the stress-strain curve of a load-cycled sample (taken from a parallel study of load cycling) which indicates that the knee is associated partly with a reduction in stiffness and partly with an irreversible strain increment. Indication of shear strain damage occurring diagonally from the hole in the 0/90 composites prior to failure was provided by a parallel study using thermal emission but also here by diagonal, stepped fracture paths in which individual fibre bundles failed in a tensile mode but away from the centre plane of the sample (Figure 7).

![Stress-strain curve of a load-cycled sample.](image1.png)

![Fracture surface showing diagonal fracture paths in 0/90 sample.](image2.png)

In Figure 8 the results of the heat-treatments have been presented in the form of a Larson-Miller plot. For treatments above 500°C the results (for a given a/w) follow a uniform trend which makes it possible to predict strength values for heat-treatments at other times and/or temperatures. The values from Jurf and Butner have also been included. The present experimental data shows good agreement with the previous results. A minor difference is seen for higher temperatures and/or times, where the material in this study shows a larger decrease in strength. This can at least partly be explained by the fact that the Jurf and Butner reported unnotched strength.
4.2. Notch sensitivity

As indicated above, the tensile fracture stress results for the 0/90 materials were analysed in terms of the Waddoups model. The basis of the model is that the fracture stress, $\sigma_F$, of a centre-hole notched infinite plate is given by:

$$K_c = \sigma_F \sqrt{\pi \left( \frac{a}{2} + c_0 \right)}$$  \hspace{1cm} (1)

where $a$ is the hole diameter, $K_c$ is a critical stress intensity factor and $c_0$ is the length of two cracks on opposite sides of and adjacent to the hole. In fibre composites it is assumed that the damage zones adjacent to the holes are equivalent to the cracks. It is also assumed that both $K_c$ and $c_0$ are constants, that is independent of hole size, for a given material. The two parameters cannot readily be related to actual physical processes in the material but provided that they are found experimentally to indeed be constants then they offer a convenient means of comparing materials as well as providing a means of strength prediction via equation 1. Thus the embrittlement of a composite can be expected to lead to a reduction of both $K_c$ and $c_0$.

In order to apply equation (1) to the present strength values, these were first corrected for the finite width effect by applying the factor $K/\beta$, where $K$ is the stress intensity factor for a hole in a plate with finite width:

$$K = 3.00 - 3.13\left(\frac{a}{w}\right) + 3.66\left(\frac{a}{w}\right)^2 - 1.53\left(\frac{a}{w}\right)^3$$ \hspace{1cm} (2)

The corrected stress value is in effect the predicted strength of an infinite plate. The width-corrected values for a nominal $a/w = 0.25$ are listed in Table 3 and for all $a/w$ they are presented in Figure 9.

The corrected values were used with equation (1) to find the $K_c$ and $c_0$ values for each treatment condition. The three $a/w$ geometries for each condition permitted three independent solutions for these constants. In almost all cases the values obtained lay very close to each other thus justifying the assumption that they were constant within the range of the
experiments. Average values for the various heat treatments are included in Table 3 together with the unnotched strength values estimated by inserting the values of the constants into equation (1) with \(a = 0\). It is seen that the constants indicate a significant embrittlement with increasing treatment time and temperature. The embrittlement is particularly noticeable at 1100°C, 100h. This is seen, not only in the low values of \(K_c\) and \(c_0\) but also as a greater notch sensitivity measured as the relative loss in fracture strength of notched samples with respect to the unnotched strength. At \(a/w = 0.25\) the loss was 65% for the 1100°C/100h material compared to 20-30% for the other treatments and the as-received material.

The constants can in association with equation (1) be used to predict the effect of notch diameter on strength of an infinite plate and these predictions are included as the curves in Figure 9. The closeness of these curves to the experimental results provides another justification of the applicability of the model.

Table 3. Strength values corrected for finite width, and the results of the application of Waddoups model.\(^21\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrected net-section strength* [MPa]</th>
<th>(K_c) [MPa (\sqrt{m})]</th>
<th>(c_0) [mm]</th>
<th>Estimated unnotched strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre orientation: 0/90°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received A (RT)</td>
<td>163</td>
<td>18.9</td>
<td>2.7</td>
<td>205</td>
</tr>
<tr>
<td>As-received B (RT)</td>
<td>140</td>
<td>17.5</td>
<td>2.2</td>
<td>210</td>
</tr>
<tr>
<td>200hrs at 500°C (B)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100hrs at 1000°C (B)</td>
<td>135</td>
<td>14.4</td>
<td>2.0</td>
<td>182</td>
</tr>
<tr>
<td>3240hrs at 1000°C (B)</td>
<td>84</td>
<td>8.9</td>
<td>1.7</td>
<td>122</td>
</tr>
<tr>
<td>20hrs at 1100°C (A)</td>
<td>92</td>
<td>9.8</td>
<td>1.7</td>
<td>134</td>
</tr>
<tr>
<td>100hrs at 1100°C (A)</td>
<td>30</td>
<td>2.7</td>
<td>0.3</td>
<td>88</td>
</tr>
</tbody>
</table>

* for nominal \(a/w=0.25\)

4.3. Microstructure and fractography

Figure 10 shows representative micrographs of the fractured, as-received 0/90 material. There were numerous cracks in the matrix perpendicular to the plies (Fig. 10a) one example being shown more closely in Figure 10b). These never penetrated the fibres. Since the density of cracks was similar in untested material it is supposed that the majority are shrinkage cracks formed during production rather than multiple matrix cracking generated during loading. The shrinkage cracks widened significantly during heat-treatment, possibly due to shrinkage of the matrix, (see below). There were large voids in some of the fibre-free areas, but also occasionally inside bundles. These large voids will in the following be denoted macropores. The infiltration into most bundles was effective, but several of them show incomplete infiltration (see Fig. 10 c) and d)).
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Fig. 9. Net section strength, corrected for finite width, versus hole diameter for 0/90 fibre orientation.

- a) Overview, optical microscope.
- b) Shrinkage crack between two fibres. (SEM, SEI)
- c) Successful infiltration in fibre bundle. (SEM, SEI)
- d) Infiltration not complete. (SEM, BEI)

Fig. 10. As-received material showing shrinkage cracks, and voids (a and b) and examples of complete (c) and incomplete (d) bundle infiltration. TW surfaces.
Overviews of the microstructure after heat-treatment for 100 hours at 1000°C and 1100°C are shown in Figs. 11a) and b) respectively. The heat-treatment caused an opening of some of the shrinkage cracks and coarsening of the macropores. Characterisation of the porosity is presented below in section 4.4. No fibre bundle fractures were found. The response of ±45° material was identical to that of the 0/90 material.

![Microstructures of material heat-treated for 100 hours at temperatures of 1000°C (a) and 1100°C (b), respectively (LT surface sections of 0/90° samples).](image)

Evidence for shear damage was sought on micrographs of the LW surfaces of fractured samples of as-received 0/90 material. Damage in the form of crack networks in the matrix that could well be attributed to shear deformation was observed in zones stretching diagonally from the hole (Fig. 12).

SEM fractographs of selected fracture surfaces of 0/90 samples are shown in Figure 13. The as-received material exhibited considerable fibre pull-out. The pulled out fibres were smooth and free of attached matrix consistent with a low ratio of interface debonding energy to fibre fracture energy. After heat-treatment at 1000°C, fibre pull-out was still extensive but significantly reduced in comparison with the as-received material. Moreover traces of matrix material sticking to fibre surfaces could be observed as well as groups of fibres sintered together. Evidence of increased matrix sticking could also be seen in the samples tested at high temperature (i.e. after very short thermal exposure). After heat-treatment for 100 hours at 1100°C the material exhibited negligible fibre pull-out (Fig. 13c)). Very short pull-out of sintered bundles could be found (Fig. 13d)).

![Possible shear damage in tested as-received sample with 0/90 fibre orientation. LW surface, optical micrograph.](image)
4.4. Density and porosity measurements

The density, porosity and microhardness measurements are summarised in Table 4. The overall dimensions and the weight of the samples and consequently their overall density did not change significantly with thermal exposure. Similarly no significant change in the open porosity was detected. However, there was a significant change in the nature of the macroporosity; the macropores tended to grow larger and some matrix cracks opened during exposure (compare Figs 10a, 11a and 11b). The macroporosity was therefore characterised quantitatively on TW sections, defining macropores as all pores with a diameter larger than 22μm or, in the case of elongated pores and cracks, lengths greater than 44μm. It was found (Table 4) that the volume fraction of macropores increased with thermal exposure and at 1100°C their average size also increased. An obvious interpretation of these results is that the matrix densified by sintering. Instead of leading to overall shrinkage of the composite which was constrained dimensionally by the fibre skeleton, the densification occurred internally by
growth of existing macropores and matrix cracks. SEM observation did indicate a reduction in the microporosity in the matrix from about 30 to 10 vol% but this was not possible to confirm with accuracy due the extreme fineness of the pores. Densification of the matrix was however indicated by an increase in microhardness.

The microhardness of the matrix increased markedly with treatment temperature and time at 1000 and 1100°C (see Table 4). At a few locations on samples treated at 1100°C and at 1000°C for 3240h very low hardness values were obtained in association with a glassy appearance of the matrix and with the formation of cracks from the corners and edges of the indent. Since SEM-EDS analysis of these locations did not indicate any significant deviation in chemical composition it is possible that large voids lay just beneath the surface in these cases. In Table 4 are listed average hardnesses and standard deviations based on ten indentations omitting these extremely low values. The scatter of the values also increased significantly after thermal exposure, indicating that the matrix became inhomogeneous. This is also indicated in the micrograph in Figure 15 where variations in porosity levels can be seen, the denser areas giving brighter reflection. Several indentations also indicated matrix embrittlement after heat treatment by the formation of indentation cracks emanating from indent corners (Fig. 16).

![Fracture surfaces of samples with ±45° fibre orientation, as-received and after heat-treatment at 1100°C.](image)

Table 4. Density, open porosity, average pore area and hardness values of the matrix as a function of heat-treatment time and temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density [g/cm³]</th>
<th>Open porosity [%]</th>
<th>Average hardness* [HV]</th>
<th>Porosity [vol%]</th>
<th>Pores per unit area</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>2.64</td>
<td>2.68</td>
<td>21.8</td>
<td>20.9</td>
<td>204 (22)</td>
</tr>
<tr>
<td>1000°C 100 hrs</td>
<td>2.60</td>
<td>2.67</td>
<td>23.2</td>
<td>20.9</td>
<td>213 (54)</td>
</tr>
<tr>
<td>1000°C 3240 hrs</td>
<td>2.64</td>
<td>2.67</td>
<td>22.7</td>
<td>20.7</td>
<td>323 (22)</td>
</tr>
<tr>
<td>1100°C 20 hrs</td>
<td>2.61</td>
<td>-</td>
<td>22.3</td>
<td>-</td>
<td>334 (33)</td>
</tr>
<tr>
<td>1100°C 100 hrs</td>
<td>2.64</td>
<td>2.62</td>
<td>22.8</td>
<td>21.8</td>
<td>457 (116)</td>
</tr>
</tbody>
</table>

* Standard deviations in parenthesis. Average taken of 10 indents.
4.5. XRD and Raman spectroscopy

The XRD investigation showed that the material in the as-received sample consisted of semi-amorphous corundum plus mullite, but after thermal exposure at 1100°C for 100 hours the amorphous fraction had disappeared and the composition had changed to corundum, mullite and cristobalite (see Fig. 17). It was also observed that the (120) and (210) mullite peaks had shifted. These observations suggest that the silica in the matrix segregates and crystallises into cristobalite. XRD spectra of the samples thermally exposed at lower temperatures or shorter time at 1100°C did not show any cristobalite peak and the amorphous fraction was retained. An additional sample exposed at 1200°C for 8 hours did not exhibit any cristobalite in the sample.

The results of the HT-XRD study of as-received Nextel 720 fibres revealed, as expected, the thermal expansion of the mullite and alumina phases. However, beginning around 900°C, the expansion coefficient of the a-axis of the mullite crystal structure (the crystal structure being close to tetragonal in the as-received fibre) began to decrease with increasing temperature and subsequently became negative, implying shrinkage of the a-axis. The resulting change in axial ratio was largely retained on cooling. At the same time changes in relative peak-intensities indicated an increase in the amount of alumina. These observations suggest the initiation of a permanent change in the fibre involving a reduction in aluminium content in the mullite associated with a shift in crystal structure from near-tetragonal to orthorhombic, an effect reported earlier by Wilson et al.26

The results of Raman spectroscopy indicated no change in the composition of the fibres after heat-treatment for 100 hours at 1100°C. Also the spectra for the matrix was very similar before and after heat-treatment, (see Figs. 18a and b)). The only difference detected in the matrix was a slightly higher content of alumina in the matrix after heat-treatment. No cristobalite was detected in the matrix or the fibres either before or after heat-treatment.
Fig. 17. Detail of XRD spectrum between 18 and 30°.

Fig. 18. RAMAN spectra for a) the fibres and b) the matrix before and after heat-treatment for 100 hours at 1100°C. Peaks are identified with the letter m for mullite and a for alumina.

5. Discussion

The mechanical test results revealed that thermal exposure of the composites at 1000°C and above caused embrittlement and, in the case of 0/90° composites, loss of strength. This degradation was particularly marked after 100h at 1100°C when the 0/90 material exhibited a fracture toughness and notch sensitivity that would be expected of a monolithic ceramic. A number of reasons for such degradation can be sought including: (i) sintering of the matrix leading to reduction in porosity and consequently a loss of the supposed crack deflection behaviour (ii) increased bonding between fibre and matrix leading to a similar effect (iii) strength reduction of the matrix due to phase changes and/or grain growth (iv) degradation of the fibre.
The porosity measurements, supported by microhardness measurements indicated clearly that matrix densification occurred during thermal exposure. The overall shrinkage of the samples was negligible due to the constraint of the continuous fibre skeleton but the shrinkage occurred internally leading to opening of matrix cracks and growth of existing voids. An increased bonding between fibres and matrix also occurred as evidenced by an increased adherence of matrix to the fibres observed on fracture surfaces. Both matrix strengthening and increased fibre/matrix bonding was indicated by the increasing stiffness of the composites. Evidence for a strengthening of the matrix and the fibre/matrix bonding is also provided by the fact that the strength of the ±45 composite, which is dominated by the matrix properties, increased while its strain to failure decreased with thermal exposure. Thus, after 100h at 1100°C the 0/90 and ±45 materials had similar mechanical properties approaching the behaviour of a monolithic ceramic.

There were some indications of phase transformation, namely the formation of cristobalite after 100h at 1100°C. This was observed by XRD but not by Raman spectroscopy. However, in the latter method spectra were taken from a restricted number of spots in the sample and could therefore have overlooked cristobalite if this existed locally. Phase studies of the alumina-silica (A-S) system show that mullite can exist over a relatively wide range of A:S ratios.\(^\text{27}\) The composition of the matrix in the present composites is considered to lie well within this range. However, if the matrix mixture were inhomogeneous, as was indicated by the metallographic studies, regions of high silica content lying outside the mullite range and therefore having a potential for cristobalite formation could have existed locally. An alternative explanation for the occurrence of cristobalite is that the matrix, prepared from an alumina-silica mixture, had not fully reacted to mullite at all places. The formation of mullite matrices in similar composites has been observed to occur via cristoballite formation at temperatures as low as 1240°C.\(^\text{28}\) Cristobalite is generally considered to be a high-temperature form of silica occurring above about 1450°C\(^\text{27}\) but could well be encouraged to form at lower temperatures by the nature of the precursor reactants and/or impurity species such as Na and K.\(^\text{29}\) In view of the local and transient nature of cristobalite in the composites it is considered that its formation did not contribute directly to the composite degradation.

Regarding the strength retention of Nextel 720 fibres after thermal exposure, the present authors are not aware of any reported measurements for exposures corresponding to the thermal treatments applied to the composites in this work. However, the HT-XRD results presented here and the few reported results of strength loss of fibres indicate that permanent structural changes can occur in the fibre and that this would be accompanied by some strength loss. Such strength loss could lead to the reduction in fibre pull-out observed on the fracture surfaces but this could equally well be attributed to the increased fibre-matrix bonding. Resolution of this question awaits further studies of fibre strength degradation due to thermal exposure.

6. Conclusions

The effects have been investigated of thermal exposure on the microstructure and stress-strain behaviour of a woven, continuous oxide fibre reinforced composite with a porous oxide matrix, the stress-strain behaviour being evaluated on centre-hole notched plates.

In the as-received condition the 0/90° orientation of the composite exhibited non-brittle behaviour and moderate notch sensitivity at room temperature, 1000°C and 1100°C. The non-brittle behaviour and low notch sensitivity could be attributed to both extensive fibre-matrix debonding and shear damage in the matrix. The ±45 orientation also had low notch sensitivity. At 1000°C it exhibited a significantly higher fracture stress and fracture strain than
at room temperature. This effect can be attributed to simultaneous sintering and creep of the matrix occurring during the test.

Thermal exposure at 1000° and 1100°C caused a progressive degradation of the composite indicated, in the 0/90° composite, by a fall in room-temperature strength and strain to failure for a given sample geometry (a/w ratio). This degradation could be described in terms of a Larson-Miller plot which consequently permitted the prediction of the strength loss for a given exposure temperature and time combination within the investigated experimental range. Thermal exposure of the ±45 composite led to an increase in its room-temperature fracture strength but also a marked embrittlement.

The embrittlement of the 0/90° material could be successfully characterised in terms of an effective fracture toughness ($K_C$) and effective damage zone length ($c_0$) derived on the basis the simple model of Waddoups et al. These parameters were constant (i.e. independent of a/w) for a given thermal exposure but decreased consistently with thermal exposure temperature and time.

Exposure for 100h at 1100°C led to almost "complete" degradation of the composite in the sense that the fracture was brittle and the values of $K_C$ and $c_0$ fell to values characteristic for a monolithic oxide while the notch sensitivity was much greater than for the lower thermal exposures. The fact that the ±45 samples exhibited similar stress-strain behaviour after the same exposure is consistent with this interpretation.

Microstructural and fractographic examination indicated that the property degradation was caused by a combination of matrix densification and increased fibre/matrix bonding. Some degradation of fibre properties could also have been a contributory factor. Formation of cristobalite was observed in samples treated for 100h at 1100°C. This was deemed to have occurred locally in the matrix and not to have contributed directly to the property degradation.

Acknowledgements

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Mechanical Behaviour of Long Sapphire Fibre / Alumina Matrix Composites

To be submitted
Mechanical behaviour of long sapphire fibre / alumina matrix composites

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Abstract
Selected mechanical properties of all-oxide composites reinforced with large diameter sapphire fibres with a porous zirconia interphase were investigated. Unidirectional and 0/90° laminates were investigated. The study included stress-strain behaviour in tension and bending, as well as characterisation of the interface by push-out testing and by analysis of the pull-out distribution of the fibres. Creep at elevated temperature was also investigated. In tension the composites exhibited a non-brittle fracture but with a fracture strength (100-200 MPa) which was below the values expected in view of the fibre strength. The pull-out was extensive due to low debonding stress and low interfacial sliding friction stress (between 2 and 10 MPa). The value of the interfacial sliding friction stress was consistent with measurements made by push-out testing of single fibres. From bending the interply and interfibre shear strengths of the unidirectional composites were found to be 14 and 23 MPa respectively. Compressive creep resistance of the UD composites was lower than predicted from values expected from uncombined fibres.

Keywords: Composites; Sapphire; Alumina

1. Introduction

All-oxide composites have potential as high-temperature material in oxidising environments, for example in turbine engines, due to their resistance to oxidation. Using a reinforcement in the form of long fibres and a suitable fibre/matrix interface, that provides a favourable path for crack deflection, can give non-brittle fracture behaviour. The creep resistance can be considerably increased by the use of single crystal fibres and even though these fibres are today considered too expensive for use in a commercial composite they do provide a model composite system for the purposes of demonstration. The objective of the present work has been to investigate a range of mechanical properties of an all-oxide composite, consisting of monocry stalline sapphire fibres in an alumina matrix, both unidirectional and with 0/90° orientation.

Sapphire fibre reinforced alumina is a thermodynamically stable system which has attracted much interest for use in severe conditions. As both constituents are of the same material the composite exhibits little thermal expansion mismatch, which minimises processing damage and degradation due to thermal shock. The fibre/matrix interface plays a vital role and several different oxides have been investigated as possible interfacial layers.

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However, not many oxides are suitable due to the amphoteric nature of alumina, i.e. it can react with both basic and acidic oxides. A mixed aluminate that is compatible with alumina and that has crystallographic planes of easy cleavage, which promotes crack deflection, is $\beta$-alumina-magnetoplumbite. However, here some fibre degradation was found due to morphological instability of the interface and fibre growth into the matrix. Mechanically weak oxide compounds that have attracted some interest are the rare-earth phosphates, for example monazite ($\text{LaPO}_4$). However, compatibility with the fibre is restricted to stochiometric monazite; an excess of La or P leads to reaction with alumina which could lead to a degradation of fibre strength. Fugitive fibre coatings have been tested with Saphikon fibres, i.e. the coating is oxidised away to create a gap along the fibre/matrix interface. Molybdenum and carbon have been used. The load transfer is dependent on the degree of fibre surface roughness. The drawbacks of fugitive coatings are poor transverse properties and the risk of local fibre/matrix reactions at contact points. A combination of an inner layer of fugitive carbon and an outer layer of zirconia has been reported by Sudre et al. After oxidising the carbon away there was a gap between the fibre and the zirconia interphase. The composite showed desirable behaviour in flexural and tensile testing.

Zirconium dioxide is chemically compatible with alumina. Some results have shown that dense zirconia as an interphase between sapphire fibres and an aluminium oxide matrix is not suitable for optimising composite toughness and strength, due to too high interfacial shear strength and interfacial friction. One solution is to use a zirconia interphase containing microporosity. Porous zirconia interphases have been obtained successfully by coating the fibres with a mixture of carbon and zirconia; after burn-out of the carbon from the consolidated composites a porous zirconia interface remains. Lundberg and Eckerbom studied model composites comprised of zirconia coated sapphire fibres in an alumina matrix and documented crack deflection in the interphase. It was also shown by Davis et al. that the zirconia interphase must be porous in order to be sufficiently weak. The fracture energy of the sapphire/zirconia interface was too high ($\Gamma_f/T_f = 0.8$) to satisfy the debonding criterion. Debonding could be encouraged by development of a porous microstructure which provides a lower energy fracture path through the coating ($\Gamma_f/T_f < 0.25$) which is considered to be a prerequisite for debonding. The interfacial shear strength of a zirconia coated sapphire fibre has been shown to decrease with increasing fibre coating thickness (from 389 to 241 MPa for 0.15 and 1.45 micron thick coatings respectively). No effect of fibre coating thickness on the interfacial sliding stress was observed.

The properties have been thoroughly investigated of sapphire reinforced alumina as a possible material for combustor tiles. Zirconia coated sapphire fibres in a hot-pressed alumina matrix exhibited crack deflection both at the sapphire/zirconia interface and within the zirconia interphase. Lewis et al. have documented a fracture stress in bending of almost 500 MPa at a strain to failure of about 0.25% in a sapphire fibre reinforced alumina matrix with a porous zirconia interphase. The stress-strain response was pseudo-ductile with limited pull-out. The debond stress in a push-out test was 14 MPa and the sliding stress ($\tau$) was about 11 MPa. A later study of a similar composite but with an interface of in-situ reacted $\beta$-alumina yielded 120 MPa and 45 MPa respectively for the corresponding parameters.

The stress-strain response of a composite with monazite coated sapphire fibres in an alumina matrix has been investigated by Marshall et al. The flexure strength was almost 150 MPa and fracture surfaces showed fibre debonding and sliding.

Reaction bonding was shown to be a successful alternative for production of sapphire fibre reinforced alumina. The compaction of the alumina powder is improved and leads to a defect-free structure of the matrix. At temperatures below 1300°C composites produced in this way with uncoated sapphire fibres exhibited crack deflection and fibre/matrix debonding. However, at temperatures above 1300°C an interphase seemed to be necessary.
Sapphire fibres (Saphikon Inc. USA) are single crystal aluminium oxide fibres oriented in the c-axis direction, produced by edge-defined film fed growth. As a result of this process, the as-received fibres have regular surface undulations perpendicular to its axis with a spacing of approximately 60 microns. Being single crystals they exhibit higher creep resistance than polycrystalline alumina fibres but the creep performance is sensitive to crystallographic orientation. The fibres exhibit a well documented drop in strength at around 300°C, followed by an increase in strength around 500°C. The strength at high temperatures and low strain rates is also reduced by slow crack growth. The cracks emanate from internal pores or from surface defects and the process is strongly temperature dependent. The 100-hour creep rupture strength for the Saphikon fibres has been shown to be less than 700 MPa in the temperature range 1100 to 1400°C. According to the manufacturer the mean tensile strength of the fibres is 3500 MPa at a length of 25.4 mm, the strain to failure is 0.8 % and the Young’s modulus 435 GPa.

2. Experimental

2.1. Materials

The composites in this investigation consisted of a polycrystalline alumina matrix, reinforced with long single crystal alumina fibres (Saphikon ™). The fibres were coated with a zirconia interphase containing carbon as a fugitive, and the composites were fabricated using a tape-casting process followed by hot-pressing. The alumina powder for the matrix (Baikowski, SM8) contained 5 vol% unstabilised zirconia powder (Degussa) to pin grain growth. A burn-out heat treatment in air was performed after consolidation in order to remove the carbon from the interphase material, leaving approximately 50 vol% porosity.

The 0/90 cross-ply composites originated from two different plates (designated plate 4 and 5) having different thicknesses of the interphase. The interphase thickness was increased in plate 5 in order to improve load transfer from the matrix to the fibres this having been found too low when plate 4 was evaluated. The characteristics of the different composite samples are collected in Table 1. (Microstructures can be seen in Figs. 10-14).

The fibres used for the cross-ply composites on the one hand and the unidirectional composites on the other were from different batches. The average diameter varied between 129 µm and 131 µm in the cross-ply composites and was 131 µm in the unidirectional composites. The fracture strength and Young’s modulus of the fibres are quoted by the suppliers as 3500 MPa (L=25.4 mm) and 435 GPa respectively. For the present work measurements were made of fracture strengths and modulus of a group of fibres from a different batch from those used for the composites. For a fibre length of 50 mm the median strength was 2620 MPa. In terms of the three parameter Weibull function the modulus m=6.1. Introducing surface damage (by measurement of fibre diameter with a micrometer) reduced the median strength to 2060 MPa but increased the modulus to m=11.5. The Young’s modulus, determined on groups of fibres with different lengths to permit correction of errors due to grip shear, yielded a value of 475 GPa.
Table 1. Characteristics of the different panels.

<table>
<thead>
<tr>
<th></th>
<th>UD</th>
<th>Plate 4</th>
<th>Plate 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre volume fraction, (V_f) [%]</td>
<td>31</td>
<td>29.5</td>
<td>29</td>
</tr>
<tr>
<td>Density [g/cm(^3)]</td>
<td>3.45</td>
<td>3.52</td>
<td>3.46</td>
</tr>
<tr>
<td>Number of plies</td>
<td>12</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Fibre diameter(^a) [(\mu m)]</td>
<td>130.9 (4.6)</td>
<td>130.9 (14.8)</td>
<td>129.0 (10.7)</td>
</tr>
<tr>
<td>Interface thickness(^b) [(\mu m)]</td>
<td>3.0 (1.4)</td>
<td>5.0 (2.8)</td>
<td>3.4 (1.3)</td>
</tr>
</tbody>
</table>

\(^a\) Measured with Archimedes technique (water). \(^b\) Average measured on cross-section of 25 fibres. Standard deviation in parenthesis.

2.2. Tensile testing

The UD material was cut into straight-sided bars with a length of 100 mm and a cross-section of approximately 3x3 mm\(^2\). To facilitate gripping end tabs of epoxy with a length of 30 mm were glued (DP 490, 3M, USA) at both ends. The bars were tested in air at room-temperature in a 4411 INSTRON mechanical testing machine. The cross-head speed was 0.5 mm/min and the extension was measured over a 20 mm gauge section using a clip-on extensometer and the load was recorded with a 5 kN load-cell.

The cross-ply material was tested using 200 mm long test bars at room-temperature. A servo-hydraulic MTS testing system with hydraulic collet grips and a cross-head displacement rate of 0.5 mm/min were used.\(^{18}\) The extensometer gauge length in this case was 25 mm. The test-bars were machined into a dog-bone shape to ensure fracture in the gauge length. Following the main failure event at the UTS further extension of the sample was recorded as machine displacement.

2.3. Bend testing

Four-point bend tests were performed in a Dartec electromechanical testing machine on UD bars cut from the composite with a diamond saw. The tests were performed in an alumina rig with 20 mm inner span and 40 mm outer span. Displacement was measured with a clip gauge attached to the upper and lower anvils of the rig. The material response was studied in two directions relative to the interply planes and with different sample dimensions (see Fig. 3) in order to favour either tensile or shear failure. The surfaces of the specimens were examined after testing to ascertain the predominate failure mode (shear or tension).

2.4. Creep

The creep of the UD material was measured in compression in air parallel to the fibre direction at temperatures between 1200 and 1400°C and stresses up to 35 MPa in the Dartec electromechanical testing machine. The samples had dimensions of approximately 3x3x7 mm and were loaded along the long axis between alumina mandrels the strain being measured by means of a high-temperature extensometer with alumina rods placed against grooves machined into the sides of the mandrels. During heating to the creep temperature and a subsequent stabilising hold time of 8 h the load was maintained at 6.4 MPa. Following this, the sample was loaded at the selected stress level for a period of at least four hours. In most
cases the sample was then loaded to increasingly higher stress levels without intermediate cooling. The test was terminated when tertiary creep began.

2.5. Pull-out length measurements

The fibre pull-out length distribution was measured using an image analysis program (Scion Image) on scanning electron pictures of the fracture surfaces of the different test-bars.

2.6. Push-out testing

Push-out tests were performed on individual fibres in thin slices of the composite using equipment described earlier. The push-out slices were cut perpendicular to the fibre direction using a high-speed diamond saw. Both slice surfaces were then polished with diamond paste down to 3 microns. A 0.06 microns colloidal silica suspension was applied as the final polishing step. Series of push-out experiments were performed on slices with a range of thickness using an 80 micron diameter flat-bottomed punch to load the selected fibres. Following the initial push-out test, the slice was turned over and the protruding fibre pushed-back.

2.7. Microstructural characterisation

The microstructure of the unidirectional and cross-ply composites was investigated using both optical and scanning electron microscopy (SEM) before and after mechanical testing. The UD material was studied prior to push-out testing. All fracture surfaces were investigated in SEM. The density and open porosity were measured with Archimedes method. The open porosity was estimated after infiltrating distilled water under vacuum for 1 hour.

3. Results

3.1. Tensile testing

Examples of the tensile behaviour of the UD and cross-ply composites are shown in Figure 1 and selected characteristic parameters are listed in Table 2. The tensile response of the UD material was linear up to about 203 MPa and 0.08 % strain after which a mild decrease of slope occurred. During this stage, audible events thought to be individual fibre fractures could be heard. The maximum stress was reached at approximately 0.08% strain and was followed by an abrupt fall in stress associated with a single matrix failure. The remaining tail of the curve was associated with separation of this single crack accompanied by fibre pull-out. There was no visible evidence of multiple matrix cracking either before or after the single matrix failure.

The two cross-ply materials were linear up to about 0.05% after which they exhibited an accelerating strain increase with increasing load. Plate 4 (thinner interfacial layer) exhibited a gradually increasing load capacity up to as high as 0.45% strain at the UTS. Following this the stress fell gradually to a tail with a very similar stress level to that of the UD composite. In a similar way this was associated with separation of a single crack and extended fibre pull-out. Plate 5 exhibited a much shorter range of strain to UTS than plate 4. Moreover the UTS
was followed by a more abrupt fall in stress to the tail marking separation and fibre pull-out. The tail was much shorter than for the UD and plate 4 composites consistent with a shorter fibre pull-out length.

![Graph](image1)

**Fig. 1.** Tensile curves of the three different composites. a) strain up to 0.5 % and b) stress versus displacement up to 1 mm (i.e. 5% strain)

The tensile properties of the test samples are shown in Table 2.

**Table 2. Summary of composite tensile properties.**

<table>
<thead>
<tr>
<th></th>
<th>UD</th>
<th>Plate 4</th>
<th>Plate 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus [GPa]</td>
<td>247</td>
<td>157</td>
<td>194</td>
</tr>
<tr>
<td>Elastic limit [MPa]</td>
<td>203</td>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>Ultimate tensile strength [MPa]</td>
<td>203</td>
<td>111</td>
<td>128</td>
</tr>
</tbody>
</table>

3.2. Bend testing

The load-displacement curves in bending were close to linear up to the maximum load where it is assumed that the main failure occurred. The load records of the bend tests were converted to maximum tensile stress and maximum shear stress using the theoretical relationships for ideal bending. The resulting curves for a burnt-out sample are exemplified in Figure 2. The ultimate strength values and appropriate failure mode as well as apparent Young’s moduli are summarised in Table 3. The direction of loading is defined in Figure 3. In those cases where the fracture was in tension it can be stated that the shear strength is not below the corresponding shear value and for shear fracture the same can be said of the tensile strength. As might be expected, the samples loaded normal to the interply planes failed in shear with relatively low shear strength. The measured tensile strengths are consistent with those measured in the tensile tests.
Fig. 2. Tensile and shear stress versus displacement curves of a burnt-out sample bend-loaded in direction 2, see Figure 3 below.

Fig. 3. Test geometry of bend bars. Fibres are oriented parallel to the 1 axis.

Table 3. Configuration of the bend test and bend testing results. The height of the specimen in the loading direction is denoted \( h \).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Burn out</th>
<th>( b \times h ) [mm(^2)]</th>
<th>Loading direction</th>
<th>Status of fracture</th>
<th>Tensile strength [MPa]</th>
<th>Shear strength [MPa]</th>
<th>Young’s modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no</td>
<td>2.35x3.35</td>
<td>2</td>
<td>tensile</td>
<td>285</td>
<td>( \geq 17 )</td>
<td>238</td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>3.35x2.30</td>
<td>3</td>
<td>shear</td>
<td>( \geq 273 )</td>
<td>23</td>
<td>207</td>
</tr>
<tr>
<td>3</td>
<td>yes</td>
<td>2.43x3.33</td>
<td>2</td>
<td>tensile</td>
<td>283</td>
<td>( \geq 17 )</td>
<td>252</td>
</tr>
<tr>
<td>4</td>
<td>yes</td>
<td>3.32x2.30</td>
<td>3</td>
<td>shear</td>
<td>( \geq 173 )</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>yes</td>
<td>5.12x3.31</td>
<td>2</td>
<td>tensile</td>
<td>264</td>
<td>( \geq 34 )</td>
<td>130</td>
</tr>
<tr>
<td>6</td>
<td>yes</td>
<td>3.30x5.03</td>
<td>3</td>
<td>shear</td>
<td>( \geq 172 )</td>
<td>14</td>
<td>155</td>
</tr>
</tbody>
</table>
3.3. Creep testing

The creep results expressed in terms of minimum creep rate are presented in Table 4. A minimum creep rate could be defined accurately only in those cases where tertiary creep had begun. In other cases the creep rate at the end of the creep curve was recorded. The creep results are also presented in the form of a Larson-Miller plot in Figure 4 where they are compared with the tensile creep of sapphire fibres. To construct the plot the value of $t$ was taken as the time that would be required to attain a creep strain of $10^{-5}$ at the recorded creep rate. Also included in the diagram is a line representing the estimated creep of the fibres in the composite based on the assumption that the fibres carried the full composite load. It is seen that the creep resistance of the fibres in the composite is inferior to that of sapphire tested in isolation. This could be due to deviations of the $<0001>$ crystallographic orientation in the fibre from the loading axis and possibly to fibre buckling. In all tests the sample expanded during the first stabilising 8 hours (load 6.4 MPa) probably due to relief of residual stresses.

Table 4. Minimum creep rates of unidirectional composite in compression.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Creep rate (6.4 MPa) [s⁻¹]</th>
<th>Creep rate (25 MPa) [s⁻¹]</th>
<th>Creep rate (35 MPa) [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>4.6 x 10⁻¹⁰</td>
<td>3.7 x 10⁻⁸</td>
<td>5.1 x 10⁻⁸</td>
</tr>
<tr>
<td>1300</td>
<td>2.5 x 10⁻⁸</td>
<td>9.9 x 10⁻⁸</td>
<td>7.2 x 10⁻⁷</td>
</tr>
<tr>
<td>1400</td>
<td>-</td>
<td>3.0 x 10⁻⁷</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig 4. Creep results presented in a Larson-Miller diagram where $T$ is creep temperature and $t$ the time taken to obtain a strain of $10^{-5}$ at the given creep rate.
3.4. Pull-out measurements

The amount of pull-out differed significantly between plate 4 and the other two composites, (see Figures 5, 6 and 7). The average pull-out length of plate 4 was almost 19 mm (median 7 mm) but for plate 5 only about 2 mm (median 1 mm). The pull-out length distribution of the UD material was similar to that of plate 5. Figure 5 shows pulled out fibres of samples of plates 4 and 5. Figure 6 shows a histogram of the pulled out lengths of the three materials while Figure 7 compares fracture surfaces of plate 5 and UD samples. It can be seen that plate 5 and the UD samples were rather similar, with a relatively high proportion of short pull-out lengths. Plate 4 material exhibited very few short pull-out lengths and a high proportion of very long lengths indicating very low interfacial bonding and friction.

Fig 5. Showing the large differences in pull-out lengths of the two cross-ply materials. Scale is in millimetres.

Fig. 6. Histogram of pulled out lengths of the two cross-ply plates and the UD material.
The interfacial friction stress, $\tau$, was derived from the load-displacement curves and the fibre pull-out distribution in the following way. Knowing the load $P_x$ the average frictional sliding stress, $\tau_x$, can be calculated at a certain crack opening length $L_x$ as

$$P_x = \pi d_f \sum_{i=0}^{n_x} (L_{\text{max}-i} - L_x) \tau_x$$

and

$$(L_{\text{max}-i} - L_x) > 0$$

for $i$ belonging to the interval $[0, n_x]$

where $d_f$ is the average fibre diameter and $\sum_{i=0}^{n_x} (L_{\text{max}-i} - L_x)$ is the total pull-out fibre length contributing to the frictional load needed at the composite crack opening length $L_x$. The symbols $n_x$ and $P_x$ are the number of fibres and the load corresponding to that length respectively.

Figure 8 shows the variation of the estimated frictional sliding stress (FSS) with the crack separation. The friction stress for all the composites falls to between 2 and 10 MPa after some separation. This level of stress is consistent with the push-out test results on individual fibres (see below). A common feature is that the friction decreases with increasing separation indicating a progressive wearing down of the interface. In the 0/90 material with thicker interphase, the friction is apparently very high at the beginning of separation. It should be noted however that the exact strain corresponding to the start of separation is not known for the 0/90 samples. Here it was assumed to occur just beyond the UTS but as discussed later it is possible that matrix failure occurred at significantly higher strain. If separation had begun just after UTS in this sample then the high apparent friction stress and the subsequent rapid decrease could be interpreted as debonding from a high bonding stress.
3.5. Push-out testing

Push-out experiments were performed on both burnt-out and non-burnt-out composites. Sets of five push-out/push-back experiments were performed successfully on burnt-out specimens. However, tests on the non-burnt-out samples proved to be impossible since the indenter failed at loads around 50 N before the fibre debonded. A detailed analysis of the interfacial behaviour can be found elsewhere. A typical load-deflection curve for push-out and the following push-back is shown in Figure 9 which also defines characteristic loads: debonding load \( P_d \), and sliding loads \( P_{d+2\mu m}, P_{d+20\mu m}, P_{d+150\mu m} \). The push-out curve can be divided into two distinct regimes, the first corresponding to the fibre debonding process assumed to end at \( P_d \). This combines the propagation of a crack along the fibre/matrix interface with friction forces acting along the debonded length. The second regime is purely frictional as the debonded fibre progressively slides out of the surrounding matrix. A complete analysis of the frictional behaviour should take into account abrasion effects that are believed to decrease the clamping stress at the fibre/matrix interface.

A similar approach as that applied for calculation of the frictional sliding stress (FSS) from the tensile test was used to derive the interfacial shear strength \( \tau_d \) and frictional stresses:

\[
\tau_d = \frac{P_d}{2\pi R t} \quad \text{and} \quad \tau = \frac{P}{2\pi R(t-u)}
\]

where \( P_d \) and \( P \) are the debonding load and the frictional load at selected fibre push-out lengths respectively, \( R \) is the radius of the fibre, \( t \) is the thickness of the composite slice and \( u \) the protruding length of fibre. Mean values of the interfacial shear stresses are listed in Table 5. It can be noted that the estimated frictional stresses after 150 \( \mu m \) sliding and during push-back are comparable with but somewhat larger than the FSS estimated from the pull-out of the tensile test. This is to be expected since Poisson dilation of the fibre occurs during push loading while Poisson contraction occurs during pull loading. Although push-out data for the
non-burnt-out material could not be obtained it can be estimated that the debonding stress must exceed 60 MPa.

![Graph showing load-deflection curve for push-out/push-back experiments on a burnt-out sample.](image)

**Fig. 9.** Typical load-deflection curve for push-out/push-back experiments on a burnt-out sample. The lower curve is the push-back curve. It is to be noted that the initial frictional load on push-back is less than the load at the end of push-out.

Table 5. Mean values of the interfacial shear stresses at debonding, debonding + 2 μm, debonding + 20 μm, debonding + 150 μm. Values shown with ± one standard deviation.

<table>
<thead>
<tr>
<th>Specimen thickness [mm]</th>
<th>$\tau_d$ [MPa]</th>
<th>$\tau_{d+2\mu m}$ [MPa]</th>
<th>$\tau_{d+20\mu m}$ [MPa]</th>
<th>$\tau_{d+150\mu m}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>22.64±1.60</td>
<td>16.92±1.38</td>
<td>10.57±1.17</td>
<td>6.42±1.27</td>
</tr>
</tbody>
</table>

3.6. Microstructure and fractography

The results from the measurement of the density and open porosity together with the assumption that the fibres were fully dense and knowing the fibre volume fraction permitted estimation of the matrix porosity and density as presented in Table 6. The closed porosity is very low which suggests that outside the large pores and cracks the matrix sinters to near full density, as is also indicated by the micrographs, shown in Figures 10 and 11.

Table 6. Porosity of the different panels

<table>
<thead>
<tr>
<th></th>
<th>UD</th>
<th>Plate 4 (TL2)</th>
<th>Plate 5 (TL16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix density* [%TD]</td>
<td>80</td>
<td>81</td>
<td>83</td>
</tr>
<tr>
<td>Matrix total porosity [%]</td>
<td>20</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>Matrix open porosity [%]</td>
<td>19.2</td>
<td>20.0</td>
<td>26.1</td>
</tr>
<tr>
<td>Matrix closed porosity [%]</td>
<td>0.9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Estimated with ROM assuming fully dense matrix has a density of 4.04 (5 vol% zirconia included)
*Based on (100-matrix density) %
*Measured value divided by fraction matrix (i.e. 1 - fibre fraction)
*Total porosity – open porosity
Micrographs of the UD and cross-ply materials are shown in Figure 10a) and b). An average grain size for the polycrystalline alumina matrix was estimated at 0.02 microns, one order of magnitude below the average interfacial zirconia grain size. A close up of the polycrystalline alumina grains and the zirconia interphase are shown in Figure 11a) and b).

Fig. 10. Cross-sections of UD and cross-ply material

Fig. 11. a) Close up of the polycrystalline alumina matrix after tensile fracture of a unidirectional tensile specimen and b) the porous zirconia interface prior to testing (SEM)

Figure 12 shows the UD material before and after burn-out of the carbon in the interface. The burn-out process clearly leads to the expected increase in porosity of the zirconia interphase. Flow lines in the matrix from the infiltration during production are also seen.
No multiple matrix cracking could be detected in any of the three composites after testing. The only cracks seen in the matrix were within a ply, between different fibres (Fig 13a) originating from production. A small number of fibre cracks were observed in all samples (Fig. 13b). However, such cracks were also observed in the cross-ply composites on sections normal to the loading direction, albeit to a smaller extent, thus indicating that some fibre fracture could have occurred prior to testing. Nevertheless the frequency of the fibre cracks was larger on the section parallel to the loading direction and this together with the fact that audible events were heard during tensile testing of the UD material indicates that some fibres broke prior to the failure of the matrix.

A variability of the fibre diameter as well as an uneven fibre distribution within the matrix are shown in Figure 14a). These micrographs also show the presence of macro porosity in the matrix as well as the presence of existing microcracks between fibres. These features are common in the processing of such composite materials.
The density in the matrix was not homogeneous as indicated by the Vickers indentations in Figure 14b). The difference was as high as almost 800 Vickers between the densest and the least dense areas (about 2000HV and 1200 HV respectively). This could be due to the constraint of the fibres on the matrix densification during production as has been explained by Lam and Lange.28

Zirconia grains could be seen on pulled-out fibre surfaces of all samples (see Figure 15 below) indicating that the debonding of the fibres takes place in the zirconia interface.

4. Discussion

4.1. E-modulus

The longitudinal modulus \(E_c\) of the unidirectional composite was approximately 240 GPa. This measured value was used to infer Young's modulus of the porous matrix (including the porous zirconia interphase). Using the standard upper bound model and an elastic modulus
for the sapphire fibre of 435 GPa\textsuperscript{29}, gave an inferred matrix modulus $E_m = 160$ GPa. This is about half of that expected for a fully dense alumina matrix with 5 vol\% zirconia (360 GPa, using the lower bound solution\textsuperscript{30}). The difference is attributable to the high matrix porosity ($p_m=20\%$). Modelling of elastic moduli of porous monolithic ceramics, showing good correlation with measurements, suggests a relationship of the form:\textsuperscript{31}

$$E_p = E_D (1 - \frac{\Phi}{\Phi_0})^n$$

(3)

where $E_p$ and $E_D$ are the moduli of the porous and fully dense materials, $\Phi$ the actual porosity (the valid range is $0 \leq \Phi \leq 0.5$) and $\Phi_0$ and $n$ are empirical correlation parameters with the values of 0.652 and 2.23 respectively. Using this expression and parameters yields a predicted matrix modulus of $\approx 170$ MPa in good agreement with the above value.

The measured moduli for the cross-ply (0/90) composites varied between 155 GPa and 194 GPa for plates 4 + 5 samples respectively. Using the standard upper bound and lower bound solutions and the matrix modulus inferred from the measured modulus of the UD composite (160 GPa), gave significantly higher calculated moduli of 220 GPa for the cross-ply composite. The lower bound expression provides a fair approximation for the transverse plies but only if fibre and matrix are well bonded and displacements are continuous across the interface, i.e. and effective load transfer occurs across the zirconia interphase.

If the assumption is made that the load transfer across the interface is small, the modulus of the transverse lamina must be described differently. A relationship for the modulus of a material with cylindrical holes aligned perpendicular to the stress axis has been given:\textsuperscript{32}

$$E = E_D \left[1 - 2 \left(\frac{P}{\pi}\right)^{1/2}\right]$$

(4)

where $E_D$ is the modulus of the dense material and $P$ the volume fraction of the holes. For a fibre volume fraction of 0.25-0.31, the modulus is now predicted to be 149-152 GPa, close to the measured value for plate 4. This estimate is thus consistent with the conclusion that plate 5 exhibited greater fibre/matrix bonding.

4.2. Debonding criteria

A prerequisite for damage tolerance in continuous fibre reinforced ceramic composites is that fibres debond from the matrix ahead of propagating cracks. The conditions for deflection of cracks can be determined by considering the energy-release rates ($G_P$ and $G_D$) associated with penetration across the interphase boundary and deflection into the boundary, respectively, as described by He and Hutchinson.\textsuperscript{33} The key material parameter dictating the ratio $G_D/G_P$ is the elastic mismatch parameter: $\alpha = (E_2 - E_1)/(E_1 + E_2)$ where $E$ is the plane strain modulus, and the subscripts 1 and 2 refer to the cracked and uncracked materials respectively. The model is assumed to be applicable to the composite system under consideration since the thickness of the zirconia interphase is small compared to the diameter of the fibres. Using the elastic moduli of the fibres and the porous matrix, the elastic mismatch relevant to cracks emanating from the matrix and then impinging on the fibres is $\alpha = 0.46$. From Figure 3 in reference \textsuperscript{33} the corresponding energy release rate is obtained: $G_D/G_P = 0.4$. Hence, crack deflection is predicted to occur when $\Gamma_D/\Gamma_f \leq 0.4$, where $\Gamma_1$ and $\Gamma_f$ are
the fracture energies of the fibre-matrix interface (in our case the porous zirconia interphase) and of the fibres, respectively.

Using experimental data on fracture toughness and elastic modulus of unstabilised zirconia with a porosity around 45 vol% \(^{34}\) and the expression for plane strain condition: 
\[ G = K_{IC}^2 (1 - v^2) / E \]
the fracture energy of the porous zirconia interphase was estimated to 0.3-2.9 J/m\(^2\). The fracture energy of the fibre is assumed to be similar to the fracture energy of sapphire, which has been measured as 12-20 J/m\(^2\), depending on the fracture plane.\(^8\) The relevant fracture energy ratio becomes \( G_f / G_p \leq 0.24 \); about half of the critical value for penetration. The conclusion is that matrix cracks should deflect into the zirconia interphase rather than penetrate into the fibres, consistent with the observed debonding in the tensile tests.

4.3. Fracture processes

The fracture behaviour of the three composites was somewhat disappointing in terms of the ultimate fracture stresses attained. On the other hand all three exhibited non-brittle behaviour due to extensive fibre pull-out. The relatively low fracture strengths are to be explained by somewhat different mechanisms in the three cases.

The UD composite was approximately linear elastic up to the ultimate stress (203 MPa). This point was marked by a sudden drop in load associated with a single violent matrix fracture. Prior to this point isolated fibre fractures could be heard to take place but these were insufficient to cause a noticeable loss of modulus. Inserting the appropriate elastic module, volume fraction and fibre radius, together with a value of 5 MPa for the interfacial friction stress and values of 10-100 J/m\(^2\) for the matrix fracture energy into the Aveston-Cooper-Kelly equation for composite stress at matrix fracture \(^{35}\) leads to values of 110-230 MPa in good agreement with the observed value. A simple shear-lag estimate indicates that the matrix fracture spacing should be of the order of the specimen gauge length which would explain why no other matrix cracks could be found. The composite stress of 203 MPa corresponds to a fibre stress of around 675 MPa. Allowing for some prior fibre fractures would rise this value but earlier studies of the effects of processing on fibre degradation indicate that such a fibre strength loss is not likely. Instead it is believed that all the fibres that remained unbroken at the point of matrix fracture failed simultaneously close to the matrix fracture surface as a result of the elastic shock wave. This is indicated by the bimodal nature of the pull-out length distribution. The previously broken fibres remained intact thereby providing the pull-out stress. The existence of such long pull-out lengths is the result of the low friction stress which yields an estimated fibre fragment length in excess of the gauge length.

Samples of plate 4 exhibited a sharp elastic limit around 90 MPa, also as a result of a single matrix fracture. The lower matrix fracture stress can be attributed to the lower volume fraction of fibres in the loading direction and possibly also the weakening effect of the transverse fibres. In this case most fibres remained intact in many cases well beyond the gauge length. The resulting large sliding interfacial area was sufficient to maintain the composite stress level over a large strain range (0.45%) before gradually decreasing.

Samples of plate 5 are believed to behave in a similar manner to the UD composite but due to a higher debonding stress the proportions of fibres failing before matrix failure was higher, leading to a measurable loss of modulus. Treating the composite as a dry fibre bundle, and assuming a Weibull modulus of 5, the ultimate composite stress would correspond to a mean fibre strength of about 1400 MPa. Again it is considered that processing would not lead to this degree of fibre degradation. It is therefore suggested that matrix failure occurred close
to the observed ultimate stress and led to premature fracture of as-yet unbroken fibres close to the matrix fracture plane.

5. Conclusions

Selected mechanical properties have been investigated of large diameter sapphire fibre reinforced alumina composites with a porous zirconia layer at the fibre/matrix interface. Unidirectional and 0/90° laminates were investigated both with fibre contents of 30 vol%.

The tensile strengths of the composites lay between 100 and 200 MPa and were below values expected in view of the fibre strength. However, the composites exhibited non-brittle failure due to extensive fibre pull-out. Both observations can be attributed to low debonding stress and low interfacial sliding friction stress. The latter was found to lie between 2 and 10 MPa, determined by measurement of the fibre pull-out length distributions. This range of values was consistent with measurements made by push-out testing of single fibres.

The interply and interfibre shear strengths of the unidirectional composite were found to be 14 and 23 MPa respectively.

The compressive creep resistance of the unidirectional composite was lower than predicted from the creep of the uncombined fibres, possibly due to poor fibre alignment and fibre buckling.

Acknowledgements

The students Miyano, Jean-Noel, Lisa and Dorit are acknowledged for participating in the mechanical testing of the material.

References

25 Manufacturers data, Saphikon, Inc., NH, USA
29 Manufacturers data, Saphikon, Inc., NH, USA.
Sammanfattning
This work has concerned the preparation and properties of all-oxide composites. The most common examples of such materials are composites of oxide particles in an oxide matrix, continuous oxide fibres in an oxide matrix and layered composites consisting of alternate layers of different oxides. In the case of continuous fibre composites, the matrix and fibres can be of the same oxide since the mechanical properties of the composite are to a large extent influenced by the interface between the two. All-oxide composites are of interest as possible high temperature materials since they are inherently oxidation resistant. The emphasis of the thesis is on continuous fibre composites. The thesis, consisting of an extensive introductory review and six appended papers (listed in appendix 2), covers a number of aspects of these composites including the properties of candidate oxide constituents, methods of composite preparation, microstructure and mechanical properties. The first paper describes attempts made to prepare alumina composites reinforced with monocrystalline (sapphire) fibres using hot isostatic pressing. The second paper reports on the thermal expansion behaviour of candidate oxides and the consequences of differences in thermal expansion of composite constituents with respect to residual thermal stresses in the composite. Paper VI reports measurements made of the stress-strain and fracture (cont.)