FIBRE REINFORCED GLASS MATRIX COMPOSITES

A REVIEW OF 30 YEARS OF RESEARCH

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SUMMARY: International research on the fabrication, properties and applications of glass and glass-ceramic matrix composites reinforced with continuous fibres is reviewed. The goal is to generate a broader interest in these composites, highlighting their high technological potential. The study reveals however that several challenges remain for future development. These include the need for better understanding of the thermomechanical behaviour of the composites and the assessment of environmental and chemical interactions under realistic in-service conditions, i.e. mostly at high temperatures. It is also emphasised that relatively limited R&D work has been carried out so far in the area of manufacturing of engineering components and of large structures with complex geometry.

KEYWORDS : Glass matrices, fibre reinforcement, high-temperature applications

INTRODUCTION

One approach to improve the mechanical properties and structural integrity of glass is to form a composite [1]. In fact Roman concrete (caementicum), used by the Romans for the construction of arches, domes and vaults, may be considered as the first structural applications of a glass containing composite material. It consisted of a mixture of silicate ash, lime and water containing stone fragments [2]. Nowadays glass and glass-ceramic materials are being considered for the fabrication of advanced composites for load-bearing structural applications at intermediate and elevated temperatures. A previous review of these materials was published in 1995 [1].

The purpose of the present review is to give an up-to-date appreciation of the underlying science and engineering of this type of composite materials, providing adequate fundamental references, and to address the prospects for the future development of these composite systems, emphasising the challenge that is involved in the exploration of new applications.

ADVANTAGES OF GLASS AS A MATRIX MATERIAL

As pointed out by Prewo [3], glass has several distinctive advantages which make it a very attractive candidate matrix material for the fabrication of composites. These include the following:

i)   glasses can be created with a broad range of chemical compositions, which allows controlling matrix/inclusion interactions;

ii) glasses can be obtained with a wide range of thermal expansion coefficients, which allows tailoring the matrix thermal expansion to match that of the reinforcing element or to introduce a controlled thermal expansion mismatch,

iii) glass powders of different chemical compositions and fine particle sizes (in the micrometer and nanometer-range) are readily available, so that powder technology, sol-gel and colloidal processing techniques can be applied to fabricate the composites,

iv) the ability to control the viscosity of glasses allow them to flow easily under low pressure at relatively moderate temperatures achieving the physical densification of composites without mechanical damage to the fibres,

v)   the ability of some glasses to crystallise can be exploited to increase their temperature capability by forming refractory crystalline phases, so that glass-ceramic matrix composites can be fabricated with application potential of up to ~1200 °C,

vi) the low elastic modulus of glasses (in the range 50-100 GPa) permits high-modulus fibres to provide true reinforcement by a load-sharing mechanism.

Besides these positive features, silicate glasses combine both economic and ecological advantages, since SiO_2 is abundant, cheap and does not pose any risk for human health or the environment. It has also been indicated [3] that glass matrices, compared with ceramic matrices, offer the greatest commercial potential for composites because of their easy fabrication, low cost and high performance at low-to-moderate temperatures.

OVERVIEW OF FIBRE REINFORCED GLASS MATRIX COMPOSITES

Carbon fibre reinforced glass matrix composites

The first paper on the fabrication and characterisation of fibre reinforced glass matrix composites was published in 1969 [4]. These composites consisted of an amorphous silica matrix containing up to 50 vol.% of unidirectional carbon fibres. Although major developments on carbon fibre reinforced glasses occurred during the 70s and 80s, especially in the United States, England and Germany [5-7], there is still scope for continued research into these composites [8,9]. Their major disadvantage is a limited capability in oxidising atmospheres at temperatures > ~ 400 ºC [10].

Nicalon® and Tyranno® fibre reinforced glass matrix composites

The development of a silicon carbide-based yarn, now known under the trademark Nicalon® (Nippon Carbon, Co.), by Yajima et al. in 1976 [11] resulted in a new group of glass and glass-ceramic composites with high temperature capability. Glass and glass-ceramic matrix composites reinforced with SiC-based fibres of the Nicalon® and Tyranno® type combine strength and toughness with the potential for high temperature oxidation resistance. This group of composites is the most fully investigated glass matrix composite system so far, as is demonstrated in the extensive available scientific literature [1,3,12-17]. Furthermore, several products have reached commercial exploitation, such as the material FORTADUR®, fabricated by the company Schott Glas (Germany) [18] and the composite Tyrannohex® produced by the company Ube Industries (Japan) [19]. Several glass matrices such as silica,

borosilicate and aluminosilicate are used, as well as glass-ceramic matrices such as lithium aluminosilicate (LAS), magnesium aluminosilicate (MAS), calcium aluminosilicate (CAS), barium magnesium aluminosilicate (BMAS) and, recently, oxynitride glass matrices have also been considered [20]. The expectation is that these matrices will provide higher temperature capability than the equivalent oxide glass matrices [20].

A distinctive member of the family of oxycarbide fibre materials is Tyrannohex®, a composite developed at Ube Industries (Japan) and based on bonded Tyranno® fibres [19, 21]. The microstructure of this composite is shown in Figure 1. The fibre volume fraction reaches values of up to 90 vol.%. Due to the near absence of a matrix phase, the material retains high strength up to very high temperatures (195 MPa at 1500°C) and it has a very high resistance to creep [21].
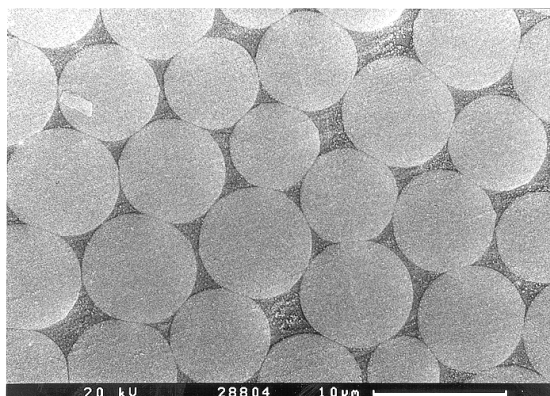

Fig. 1 SEM micrograph showing the microstructure of Tyrannohex® composite [19]. Note the high fibre volume fraction of this composite.

SiC and boron monofilament reinforced glass matrix composites

Monofilament SiC fibres (e. g. type SCS-6) have been used for reinforcement in different glass matrices [22], including model composites with transparent matrices [23,24]. Researchers at NASA Lewis Research Centre have been interested in using SiC monofilaments for the reinforcement of glass-ceramic matrices of refractory composition, including strontium aluminosilicate (SAS) [25] and barium aluminosilicate (BAS) [26], with a temperature capability of up to 1600 °C.

Glass matrix composites with oxide fibres

Alumina and mullite fibres (Nextel®-type) have been incorporated into borosilicate, LAS and other glass-ceramic matrices [27-29]. This group of composites has been developed primarily for applications above 1000°C, however, because of the strong chemical bond which usually occurs at the fibre-matrix interface, these composites showed a poorer flaw tolerant behaviour than SiC-fibre reinforced materials. To overcome this problem several coating approaches for the fibres were tried, with the aim of providing relatively weak fibre-matrix interfaces. A refractory material suggested for coating alumina fibres is SnO_2. Chawla et al. have established the principles of interface engineering for oxide fibre reinforced glass matrix composite materials, as shown in Figure 2 [30].
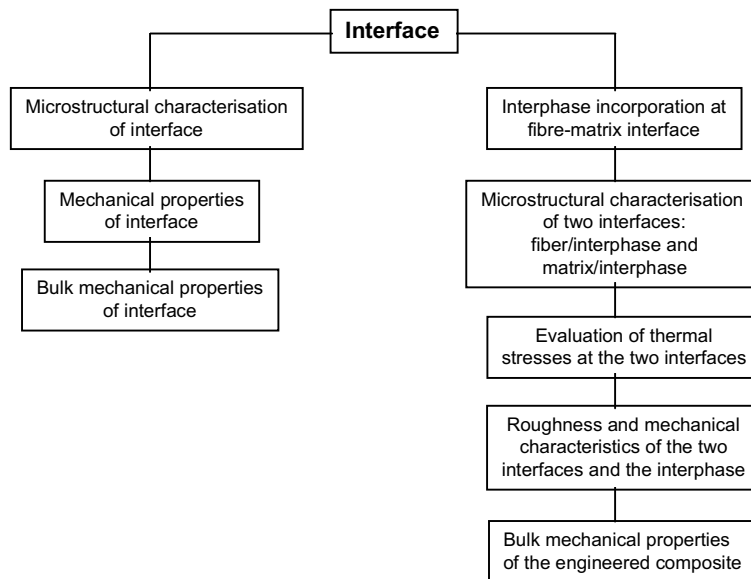
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Fig. 2 Interface engineering concept for oxide fibre/glass matrix composites [30]

Glass fibre – glass matrix composites

The development of optically transparent or translucent materials showing high fracture toughness and adequate flaw tolerant behaviour is the goal of research in the area of glass-glass composites. Recently, the fabrication of a continuous oxynitride glass fibre reinforced SiO_2-B_2O_3-La_2O_3 glass matrix has been reported [31]. Pioneering work on silicate glass matrix composites containing continuous silicate glass fibre reinforcement has been conducted in Germany [32]. The interface of amorphous glass-glass composites has to be engineered in order to avoid strong fibre-matrix bonding due to chemical reactions during composite fabrication.

Metal fibre reinforced glass matrix composites

Few reports on continuous ductile reinforcement of glass matrices have been published so far. In an earlier study, Ducheyne and Hench fabricated composite materials with a bioactive glass matrix and stainless steel fibres by an immersion technique [33]. The group of Donald et al. has reported on the fabrication of glass and glass-ceramic matrix composites reinforced by stainless steel and Ni-based alloy filaments [1,34]. These materials exhibited flexure strengths of the order of 700 MPa and very high values of work of fracture (~ 50 kJ/m^2) [1,34]. Another interesting aspect of this work has been the application of the Taylor-wire process for the fabrication of fine glass-encapsulated metal filaments [34]. Russian researchers have pioneered the use of 2-dimensional metal fibre structures to reinforce glass-ceramics [35], however only a limited number of matrices and metallic fibre reinforcements were tried. Boccaccini and co-workers have used electrophoretic deposition to fabricate a number of glass matrix composites containing 2-dimensional metal fibre reinforcement [36,37].

FABRICATION TECHNIQUES

Ease of fabrication in comparison with polycrystalline ceramic matrix composites is one of the outstanding attributes of glass and glass-ceramic matrix composites. This is due to the ability of glass to flow at high temperatures in the same way as resins.

Hot-pressing of infiltrated fibre tapes or fabric lay-ups is the most extensively used technique to fabricate dense fibre reinforced glass matrix composites [3]. For a proper densification, the time-temperature-pressure schedule during hot-pressing must be optimised so that the glass viscosity is low enough to permit the glass to flow into the spaces between individual fibres within the tows. Using 2-dimensional reinforcement (i.e. woven fibre structures) articles with complex shapes can be fabricated by the basic hot-pressing operation [18, 27, 38].

Efforts have also been made to evaluate the use of the polymer precursor method for processing these materials. In particular a novel precursor synthesized in one step from BaO, Al(OH) and SiO_2 was used to fabricate BAS and SAS glass-ceramic matrix composites [39]. In general, the precursor approach provides glass-ceramics by low temperature processing methods with good control of chemical and phase homogeneity. Another method of fabricating unidirectional fibre reinforced glass matrix composites is based on pulltrusion, as shown schematically in Figure 3 [40]. Since the fibres are exposed for only short time at high temperature (5-10 minutes), fibre degradation and fibre/matrix interaction can be minimised.

Sol-gel processing routes have been investigated as possible alternatives to the slurry method [41]: using the sol-gel approach, matrices are produced from metal alkoxide solutions or colloidal sols as precursors.
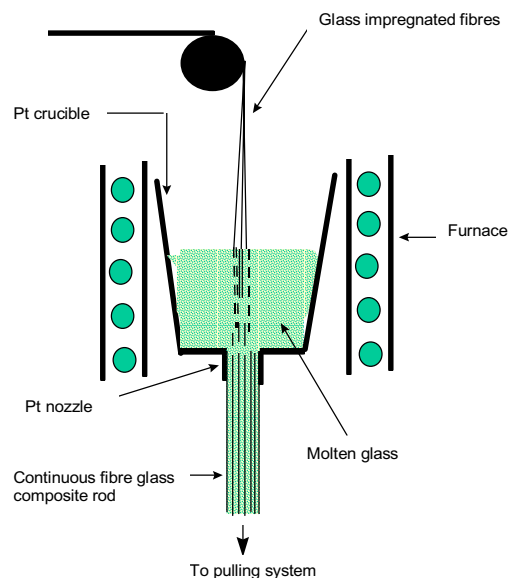

Fig 3 The pulltrusion method for the fabrication of unidirectional fibre reinforced glass matrix composite rods, according to Johnson et al. [40].

MECHANICAL PROPERTIES

The primary aim of fibre reinforcement of glass and glass-ceramics is to achieve high toughness while retaining high fracture strength. The basic approach to increasing the resistance of brittle materials to catastrophic failure is by increasing the crack propagation area. In composite materials, this is achieved by providing "weak" planes within the material in a direction parallel to the tensile stress, i.e. perpendicularly to the plane of propagation of a mode I crack, so that the crack can be deflected. In fibre reinforced composites, these "weak" crack paths are given by the fibre-matrix interfaces.

A key aspect for the success of glass matrix composites is therefore the presence of a "well-behaved" interface. For the composites reinforced by oxycarbide fibres, the interface usually forms *in-situ* during processing. Detailed high-resolution electron microscopic investigations have been conducted to elucidate the phase structure and microchemical composition of the fibre-matrix interfacial region in a variety of composite systems [42]. These investigations have shown that the interfacial zone is occupied by a carbon-rich thin layer of thickness 10-50 nm. Figure 4 is a TEM image showing the interfacial region in a Nicalon® fibre reinforced borosilicate glass matrix composite [43]. The carbonaceous layer is weaker than the matrix and the fibres and is therefore effective in deflecting matrix cracks and promoting fibre pull-out during composite failure.
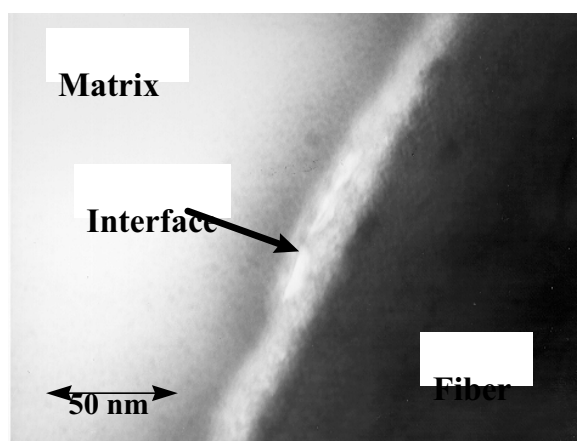

Fig. 4 TEM micrograph showing the interfacial zone in a SiC-Nicalon® fibre reinforced borosilicate glass matrix composite [43]. The carbonaceous interphase is clearly observed.

The quantitative principles of interface design in fibre reinforced glass matrix composites have been discussed in the literature [42, 44] and the toughening mechanisms active in these composites have been studied extensively in the last 15 years. The major processes contributing to the fracture toughness (work of fracture) of fibre reinforced composites are crack bridging, fibre pull-out and debonding [45,46].

When using SiC-based fibres of the type Nicalon® and Tyranno®, the temperature capability of the composites depends strongly on the environment. In oxidative atmospheres (i. e. hot air), the stability of the carbon-rich fibre-matrix interface represents the limiting factor [43]. Embrittlement and concurrent strength and toughness degradation occur as a result of

oxidation of the carbon layer and its replacement by a glassy oxide layer that is bonded firmly to both fibre and matrix, thus inhibiting matrix crack deflection at the fibre/matrix interface as well as fibre pull-out [42,43]. One way to alleviate the problem of degradation of the carbon layer at high-temperatures is to use protective coatings on the fibres [42, 47].

APPLICATIONS

Fibre reinforced glass matrix composites are light materials with suitable mechanical and thermal properties for applications in gas turbines and other specialised areas requiring high oxidation and corrosion resistance at high temperatures. Since these materials have approximately half the density of most Ni-based alloys, significant weight savings are possible in components for aerospace applications, including thermal protection shrouds, leading-edges and rocket nozzle inserts [29, 48].

The development programmes of the last 30 years have been successful in proving the impressive material capabilities of fibre reinforced glass and glass-ceramic matrix composites [49]. However, cost-effective manufacturing technologies required to fabricate real component shapes (e. g. turbine blades) and complex structures have not as yet been developed and only very limited work has been devoted to the development of machining and joining techniques [50], so that the application of these materials in most of these areas remains an open question for the future.

Another possible application for fibre reinforced glasses and glass-ceramics is in the area of anti-ballistic protection and similar impact-resistant structures [51]. In this application fibre reinforced materials with higher toughness and spalling resistance than monolithic ceramics can offer a significant advantage for use in tanks and armoured personnel vehicles. Most work developed in this area however is classified and very little has been published in the open literature.

There is a wide range of possibilities for applications of glass and glass-ceramic matrix composites in conventional technologies, i. e. at low to moderate temperatures and under low to moderate stresses. These applications may include: components for pump manufacture (e.g. vanes, bearings and seals), automotive applications (e.g. brake and gear systems), and construction of special machinery, (e. g. tools and components for use in hot environments).

Fibre reinforced glass matrix composite products are being used with commercial success for example in the area of hot glass and metal handling [18]. Preliminary results in the field of wear resistant materials for automotive applications show that the materials may have potential for use in brake and gear systems but no further data have been published so far. Similar conclusions can be drawn from our own recent investigations into the dry friction behaviour of carbon fibre reinforced glass matrix composites under conditions found in vacuum pump seals [52]. Since carbon fibres impart a certain degree of lubricity, the composites exhibit a low coefficient of friction and relatively high wear resistance [8,9].

Glass matrix composites have also been proposed for a variety of thermal stability applications, for example in support structures for laser mirrors and other precision components requiring high shape and dimensional stability and tolerances. Multidimensional zero-thermal-expansion materials can be achieved by using cross-ply carbon fibre structures in borosilicate matrices [8].

Nicalon® fibre reinforced glass matrix composites have also been suggested as substrates for electronic packages [53]. The optimum thermal conductivity and dielectric constant at 1 MHz, coupled with high fracture strength and toughness, would be attractive properties for this application. Low dielectric loss, fibre reinforced glass matrix composites have also been envisaged for Rf transmission window applications [54]. Analysis of the literature reveals however that no significant research has been conducted regarding functional applications of fibre reinforced glass and glass-ceramic composites and this research area remains as one of the most interesting challenges for the future.

The biomedical field offers another attractive area for application of these materials. Fibre reinforcement could be used to increase the mechanical properties of bioactive glass for example with the aim of fabricating load-bearing implants [55]. Fibre reinforcement may provide the necessary structural integrity but the biocompatibility of the composite must also be achieved. Preliminary investigations showed no difference in the tissue-implant interfacial behaviour of bulk bioactive glass and metal fibre reinforced bioactive glass implants after four months of implantation in beagle dogs [55]. These are encouraging results which indicate potential for innovative developments in this area.

CONCLUDING REMARKS

The various aspects of the fabrication, characterisation and applications of fibre reinforced glass matrix composites reviewed here, reveal that while considerable effort has been expended on improving the materials, much less work has been done on the development of component design methods. There is also a need for easily repeatable, automated and cost-effective processing techniques. Highly innovative development work in the area of manufacturing technology is required, including development of adequate machining and joining technologies. The development of novel glass matrix composites with improved mechanical properties, attained by fibre reinforcement and exhibiting the desired functional property which may be achieved for example by dispersion of a suitable particulate phase in the matrix, may open new application fields for these materials. Overall, as in many other advanced materials technologies, a closer collaboration and interrelationship between materials scientists, engineers, designers, technologists and users should be pursued.

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