

# Review

## Ceramic-matrix composites

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Ceramic materials often exhibit a combination of useful physical and mechanical properties, including high refractoriness, but their applications are restricted due to their brittle behaviour; in an attempt to improve the strength, and particularly the toughness, of brittle ceramics particle-strengthening and fibre-reinforcement have been utilized, with limited success. The factors which affect the mechanical properties of these composite systems are discussed, and the various experimental systems that have been investigated are reviewed. It is concluded that, although the potential applications of such materials are extremely diverse, several important aspects, particularly the effect that matrix microcracking may have on the mechanical and thermal stability of reinforced-ceramic systems, must be fully evaluated before ceramic-matrix composites can seriously be considered as useful replacements for more conventional materials.

### 1. Introduction

During recent years there has been an increasing demand for high-performance materials for use in a diverse range of applications from aerospace and military to biomedical. Particular interest has been shown in materials for limited or extended service at elevated temperatures. Unfortunately, conventional precipitation-hardened metal alloys are not thermally stable and the precipitation may coarsen at temperatures significantly below the softening point of the alloy, resulting in a decline in mechanical strength [1]. The newer class of dispersion-strengthened metals are more stable, but generally lack adequate ductility at low and intermediate temperatures, and hence are notch-sensitive and prone to catastrophic failure [2]. Further, it has now been recognized that metallic-matrix composites reinforced with ceramic fibres may be susceptible to thermal degradation, particularly under conditions of thermal cycling, due to differential fibre-matrix expansion which may lead to interface failure or even fibre fragmentation during service [3-6]. In contrast, many ceramics and glasses exhibit relatively high strength and stability at elevated temperatures, combined with low density and chemical inertness. However, owing to

the absence of significant stress-relieving mechanisms at low and intermediate temperatures these materials are notch-sensitive and brittle, and are susceptible to thermal shock [7-14].

In an attempt to increase the strength, and particularly the work of fracture and hence toughness of ceramic materials, barriers to crack propagation in the form of discrete particles or fibres have been incorporated into ceramic matrices, with limited success and this review is intended to summarize the progress that has been accomplished. The major theories that have been proposed to account for the mechanical behaviour of reinforced glasses and ceramics are first outlined and the factors which influence the mechanical properties at ambient and elevated temperatures discussed. This is followed by a review of experimental systems, which includes a summary of the fabrication techniques that have been employed to produce such materials, and an interpretation of their mechanical properties based on the thermal expansion mismatch between fibre and matrix. The final section outlines the potential applications that reinforced glasses and ceramics might eventually hope to fulfill.

## 2. Theory of reinforcement

### List of symbols

$\sigma$ ,	tensile stress
$\epsilon$ ,	tensile strain
$\tau$ ,	shear stress
$E$ ,	elastic modulus
$\alpha$ ,	linear thermal expansion coefficient
$\nu$ ,	Poisson's ratio
$\gamma$ ,	work of fracture
$V$ ,	volume fraction
$r$ ,	radius
$l$ ,	fibre length
$l_c$ ,	fibre critical length
$\Delta$ ,	differential value

### Subscripts

m,	matrix
p,	particle
f,	fibre
c,	composite
u,	ultimate
t,	theoretical
e,	experimental

### 2.1. Dispersion-strengthened materials

Strengthening by incorporation of a fine dispersion of second-phase particles has long been utilized for metallic systems. The particles may be produced *in situ* by precipitation of a secondary phase, or may be added directly by powder metallurgy techniques. These systems have been reviewed in detail by Kelly and Nicholson [15], and Ansell [16], and strengthening is attributed to various dislocation impediment mechanisms.

Dispersion-strengthened ceramics may also be produced by similar techniques. However, since dislocation mobility is already extremely low [17], particle dispersions would not be expected to contribute very significantly to an increase in strength; similarly no strength increase would be expected for non-crystalline glasses in which dislocations, as conventionally defined, do not exist. The fact that significant strengthening has been observed for certain systems in this category has been attributed by Hasselman and Fulrath, and Nivas [18,19], to the dispersion limiting the size of Griffith flaws thereby raising the stress required to initiate or propagate a crack. More recently it has been proposed that strengthening may occur as a result of a line-tension effect due to particles initially pinning a propagating crack front and causing it to bow out between

the obstacles [20–22], in a similar manner to that observed for dislocations [23]. A further mechanism may be operative if particles of higher elastic modulus than the matrix are employed, due to the effective increase in modulus of the composite relative to that of the unreinforced matrix [24]. Since this latter mechanism depends on effective stress-transfer to the dispersed phase, a strong particle-matrix bond is essential. A fine dispersion of particles may also inhibit grain-growth during fabrication and hence lead to an apparent increase in strength [25]. Further, under suitable conditions, the effect of thermal expansion mismatch may be utilized to promote strengthening; if  $\Delta\alpha$  is negative, and the particle-matrix interface can support the resulting radial tensile stresses on cooling from the fabrication temperature, the surrounding matrix will be subjected to tangential compressive stresses, and the matrix may be strengthened. If, however,  $\Delta\alpha$  is positive, induced tangential tensile stresses may weaken the matrix, and in the limit matrix microcracking will be initiated. The resulting radial and tangential stresses,  $\sigma_r$  and  $\sigma_t$  respectively, may be assessed using Selsing's equation [26]:

$$-\sigma_r = 2\sigma_t = \frac{\Delta\alpha \Delta T}{(1 + \nu_m/2E_m) + (1 - 2\nu_p/E_p)} \quad (1)$$

If  $\Delta\alpha$  is positive, matrix microcracking is expected when the value of  $\sigma_t$  exceeds the tensile strength of the matrix.

Finally, Gupta [27] has recently suggested that strength and toughness can only be increased concurrently if second-phase particles are well bonded to the matrix and exhibit a critical strain energy release rate which is greater than that of the matrix.

### 2.2. Fibre-reinforced materials

#### 2.2.1. Factors affecting strength

The general theory of fibre reinforcement suggests that significant strengthening will only occur if the elastic modulus of the fibres is greater than that of the matrix, and if tensile stresses can be transmitted to fibres. If fibres of lower modulus are employed, the ultimate failure stress will be reduced because the matrix rather than fibres will carry a greater proportion of the applied load. Table I summarizes the properties of typical fibre and matrix materials.

The high strength and failure strain, relative to the bulk material, of high-modulus ceramic fibres may readily be exploited by incorporation into a ductile and protecting matrix, which serves the rather indirect role of binding the fibres together and providing barriers to crack propagation between individual fibres. Stresses may be transmitted to the fibres by plastic or elastic deformation of the matrix. In the absence of internal stresses the strength,  $\sigma_c$ , of a continuous fibre-reinforced composite may be estimated by the rule of mixtures criterion, assuming the strains in each component are equal, either as:

$$\sigma_c = \sigma_{fu} V_f + \sigma'_m V_m \quad (2a)$$

or as:

$$\sigma_c = \sigma'_f V_f + \sigma_{mu} V_m, \quad (2b)$$

where  $\sigma'_m$  is the matrix stress at the fibre failure strain and  $\sigma'_f$  is the fibre stress corresponding to the matrix failure strain, depending on which component fails first, and assuming that composite failure occurs immediately succeeding failure of one of the components.

For discontinuous reinforcement the ultimate strength of a given fibre can only be utilized if it lies parallel to the tensile axis, and its length exceeds a critical length, defined as the minimum fibre length in the composite which can just be loaded to its failure stress. If the fibre length is much greater than the critical length, the strength of the composite will be of the same order as that of the continuous case, and can be approximated by Equation 2. However, if the length is of the same order as, or is less than, the critical length,  $\sigma_f$  must be replaced by a mean fibre strength  $\sigma'_f$ , since the stress in the fibre varies along its length, reaching a maximum at its centre. If randomly oriented fibres are employed the proportion of fibres capable of loading to their fracture stress will be reduced, and hence the ultimate strength of the composite will be lower than that of the aligned system. Suitable "efficiency" factors have been derived to take into account the effect of fibre orientation and length, although a knowledge of the critical length is required in order to predict the length efficiency factor [28, 29]. More detailed reviews of the theoretical concepts are given elsewhere [30–32].

On the basis of the above criteria there would seem to be only very limited scope for strengthening a high-modulus brittle ceramic which exhibits

neither plastic flow nor extensive elastic deformation by the fibre-reinforcement mechanism; in addition the low failure strain of the matrix would apparently further limit the usefulness of such composites. However, it has been shown that the actual failure strain of brittle matrices (of relatively low modulus) should theoretically be increased by addition of a higher modulus fibre. After the new failure strain of the matrix has been reached, ultimate failure of the composite proceeds by a process of progressive multiple matrix micro-cracking, and the stress-strain curve usually continues to rise.

Romauldi and Batson [33] were first to propose that the cracking strain of concrete should be increased by incorporation of fine fibres. They suggested that the fibres limit the length of cracks during the early stages of initiation from pre-existing flaws due to fibres ahead of the crack tip opposing elastic displacements of the matrix. They unrealistically assumed that the fibres were perfectly bonded to the matrix and were infinitely stiff, and the high failure strains predicted have not been realized in practice.

More recently, Aveston *et al.* [34] have shown that with continuous, small diameter fibres frictionally bonded to the matrix, the failure strain of the matrix may be given by:

$$\epsilon_m = \left( \frac{12\tau\gamma_m E_f V_f^2}{E_c E_m^2 r V_m} \right)^{\frac{1}{3}}, \quad (3)$$

where  $\tau$  is the frictional bond strength. Their theory proposes that the reinforcement opposes the actual displacements of crack surfaces, and it is more in line with experimental data; the theory has also been modified for the case of discontinuous random reinforcement [35]. Both theories predict a cracking strain proportional to the inverse square root of the inter-fibre spacing and have been shown to be inter-related [36]. More recently, Aveston and Kelly [37] have shown that with well-bonded systems, the interfacial region would be unlikely to withstand the imposed shear stresses when the matrix cracks, and either the interface should fail or the matrix adjoining the interface should fail in shear. Because these major theories, based on multiple cracking of the matrix prior to ultimate failure, assume matrices of relatively low modulus, they unfortunately offer little prospect for substantial strengthening of high modulus ceramics. A third

TABLE I Comparison of some general properties of various matrix and fibre materials

Materials	$E$ ( $\text{MN m}^{-2} \times 10^4$ )	Tensile strength ( $\text{MN m}^{-2}$ )	$\alpha$ ( $^{\circ}\text{C}^{-1} \times 10^{-6}$ ) (20 to $1000^{\circ}\text{C}$ )	Density ( $\text{g. cm}^{-3}$ )	Melting point ( $^{\circ}\text{C}$ )	Comment and references
<i>Matrix</i>						
Epoxy resin	0.2-0.4	35-97	-	1.1-1.2	-	heat distortion temp. $79-218^{\circ}\text{C}$ [145]
Polyester resin	0.2-0.5	34-69	90 ( $20^{\circ}\text{C}$ )	1.1-1.4	-	heat distortion temp. $46-190^{\circ}\text{C}$ [145]
Portland cement	0.7-2.8	2.8-14	12-20 ( $20^{\circ}\text{C}$ )	1.7-2.5	-	[89]
Soda-lime glass	6.0	100 (MOR)	8.9 ( $20-480^{\circ}\text{C}$ )	2.5	-	[110, 117]
Borosilicate glass	6.0	100 (MOR)	3.5 ( $20-520^{\circ}\text{C}$ )	2.3	-	[110, 117]
Lithium aluminosilicate glass-ceramic	10.0	100-150 (MOR)	1.5	2.0	-	[110, 117]
Silica glass	7.2	48 (MOR)	0.5	2.2	1710	devitrifies $1100^{\circ}\text{C}$ [92, 140, 141]
<i>Magnesium aluminosilicate glass-ceramic</i>						
Mullite	11.9	110-170 (MOR)	2.5-5.5	2.6-2.8	1410	[39]
ThO <sub>2</sub>	14.3	83 (MOR)	5.3	-	1810-1830	[122, 140]
ZrO <sub>2</sub>	14.5	97	9.5	9.8-10.0	3050-3300	[140, 141]
MgO	17-25	113-138	7.6	5.6-5.75	2677-2710	[140]
Si <sub>3</sub> N <sub>4</sub>	21-30	97-130	13.8	3.6	2800	[140, 141]
	30.7	410	2.87 $\alpha$ 2.25 $\beta$	3.2	1900	oxidizes in air $> 1400^{\circ}\text{C}$ [79, 126, 140]
BeO	29.5-38	130-240	9.1	3.0	2520-2550	[140, 141]
Al <sub>2</sub> O <sub>3</sub>	36-40	250-300	8.5	3.9-4.0	2015-2050	[140, 141]
SiC	40-44	310	4.8	3.2	2200-2500	oxidizes in air $> 1400^{\circ}\text{C}$ [126, 140, 141]
ZrC	19.5-48	110-210	6.7	6.4-6.9	3175-3540	oxidizes in air $> 980^{\circ}\text{C}$ [140]
HfO <sub>2</sub>	56.5	69 (MOR)	5.9	9.7	2777-2812	[140]
WC	54-70	345	4.9	15.6-15.8	2627-2900	oxidizes in air $> 500^{\circ}\text{C}$ [140, 141]
<i>Fibre</i>						
Nylon 66	0.5-0.7	827-1030	-	1.1	-	typical diameter $25\mu\text{m}$ , [142]
E-glass	6.9-7.2	1700-3500	6.0 ( $25-600^{\circ}\text{C}$ )	2.6	650	typical diameter $25\mu\text{m}$ , [144]
Silica glass	7.2	5930	0.5	2.2-2.5	1710	typical diameter $1-20\mu\text{m}$ [30, 144]
BN	8.6	-	13.3	2.2-2.3	2720-3000	oxidizes in air $> 1100^{\circ}\text{C}$ [140]
Niobium	8.3-12.4	517-1034 (bulk)	8.1	8.6	2517	oxidizes in air $> 600^{\circ}\text{C}$ [140, 142]
Copper	12.4	414	19.9	8.9	1083	typical diameter $150\mu\text{m}$ [142]
Hafnium	13.8	450-590 (bulk)	6.0	13.1-13.3	2020-2230	[140]
ZrO <sub>2</sub>	15.0	1200	-	-	-	[146]
Mullite	13.8-17.8	1380	-	-	-	diameter $1.8\mu\text{m}$ [111]
Tantalum	18.6	330-1380 (bulk)	7.0	16.6	2850-3000	oxidizes in air $> 500^{\circ}\text{C}$ [140]
Stainless steels	15-21	2048-2552	-	7.7-8.0	1435	typical diameter $150-180\mu\text{m}$ [30, 142]
Plain-carbon steels	19-21	2030-3966	-	7.8-8.0	-	typical diameter $150-600\mu\text{m}$ [30, 50]
Nickel	21	530-559	17.1	8.8-8.9	1455	oxidizes in air $> 800^{\circ}\text{C}$ typical diameter $450-1110\mu\text{m}$ [50, 140]

TABLE 1 continued

Materials	$E$ ( $\text{MN m}^{-2} \times 10^4$ )	Tensile strength ( $\text{MN m}^{-2}$ )	$\alpha$ ( $^{\circ}\text{C}^{-1} \times 10^{-6}$ ) (20 to $1000^{\circ}\text{C}$ )	Density ( $\text{g. cm}^{-3}$ )	Melting point ( $^{\circ}\text{C}$ )	Comment and references
<i>Matrix</i>						
Carbon II	23-31	2415-3100	0 (axial) 8 (radial) 18.5	1.72-1.77	-	oxidizes in air $> 450^{\circ}\text{C}$ typical diameter $8\ \mu\text{m}$ (morganite) typical diameter $1780\ \mu\text{m}$ [30, 140, 142]
Beryllium	25-31	1100	18.5	1.85	1277-1330	oxidizes in air $> 500^{\circ}\text{C}$ catastrophic oxidation $> 650^{\circ}\text{C}$
Molybdenum	32	2200	5.8	10.0	2610-2630	Typical diameter $25-150\ \mu\text{m}$ catastrophic oxidation in air $> 800^{\circ}\text{C}$
Tungsten	34-41	2900-3793	4.8	19.3	3340-3410	typical diameter $25-150\ \mu\text{m}$ [30, 140, 142]
Carbon I	35-41	1380-2070	as CH	1.90-1.94	-	as CH
Boron	41-44	2800-3400	8.2	2.3-2.6	2050-2300	typical diameter $75-125\ \mu\text{m}$ [30, 36, 143]
SiC	48	2100	4.8	3.35	-	typical diameter $100\ \mu\text{m}$ [39]

theory [38] suggests that for systems of small inter-fibre spacing the fibres will limit the size of Griffith flaws in a similar manner to that proposed for particle dispersions. However, Kelly [36] discounts this theory, suggesting that if this were the case, the cracking strain should be altered by making a scratch on the surface which is greater in length than the inter-fibre spacing, and this has not been reported experimentally. Another approach is to pre-strain the matrix in compression so that a greater overall strain has to be employed to bring the matrix to its normal failure strain. This may be accomplished by utilizing fibres of higher thermal expansion than the matrix [39], but the effect is lost at temperatures approaching the fabrication temperature, and it is also dependent on the formation of a strong fibre–matrix bond.

The differential thermal expansion is a very important parameter in any composite system since it determines the residual stress–strain distributions after fabrication, and can have significant effects on the resultant mechanical properties. Four possibilities exist for a given uni-directionally aligned fibre system; defining  $\Delta\alpha$  (axial or radial direction) =  $\alpha_m - \alpha_f$  (axial or radial), these may be briefly summarized as follows:

(i) Axial direction,  $\Delta\alpha$  positive: on cooling from the fabrication temperature the fibres will endeavour to keep the matrix in tension in the axial direction. If the differential is large enough the failure strain of the matrix may be exceeded and a network of fine microcracks will develop in a direction perpendicular to the fibre axes.

(ii) Axial direction,  $\Delta\alpha$  negative: two effects are possible depending on the strength of the fibre–matrix interface. If the interface is strong enough the fibres will endeavour to strain the matrix in compression in the axial direction; this will increase the overall strain required to initiate failure and hence will result in an increase in strength. Conversely, the fibres will be subject to tensile stresses which must be taken into account when selecting a suitable fibre. For a given system, the ultimate strength will be achieved when the failure stress of the fibre is reached simultaneously with the matrix failure strain. However, if the interface cannot support the induced stresses little or no matrix pre-stressing will occur, and voids may be initiated at the ends of the fibres.

(iii) Radial direction,  $\Delta\alpha$  positive: in this in-

stance, the fibre–matrix interface will be in compression and this could produce strengthening of the chemical or frictional fibre–matrix bond. However, although this effect is desirable in itself it is usually produced in conjunction with the first case.

(iv) Radial direction,  $\Delta\alpha$  negative: this is the converse of the third case, and the interface will be subjected to tensile stresses which if strong enough may result in interfacial decohesion; hence, this will unfortunately tend to limit the useful exploitation of the second case.

The residual thermal strain,  $\epsilon'_m$ , experienced by the matrix when uni-directionally aligned fibres of differing thermal expansion are employed may be assessed quantitatively (assuming interfacial decohesion does not occur when  $\Delta\alpha$  is negative) as:

$$\epsilon'_m = \frac{E_f V_f \Delta\alpha \Delta T}{E_c} \quad (4)$$

If the value of  $\epsilon'_m$  is positive the matrix will be in tension; and this will give rise to a microcracked system if  $\epsilon'_m \geq \epsilon_m$ , where  $\epsilon_m$  is the normal failure strain of the unreinforced matrix. Conversely, if  $\epsilon'_m$  is negative, the matrix will be in compression.

For a given system, the composite failure stress,  $\sigma_c$ , may be given by:

$$\sigma_c = E_c (\epsilon_m - \epsilon'_m) \quad (5)$$

assuming the rule of mixtures criterion is obeyed, and  $E_c = E_m V_m + E_f V_f$ .

The corresponding strain experienced by the fibre is given by:

$$\epsilon'_f = \frac{-E_m V_m \Delta\alpha \Delta T}{E_c} \quad (6)$$

and the optimum strength for a given system corresponds to the situation where the failure stress of the fibre is reached simultaneously with the failure strain of the matrix.

### 2.2.2. Factors affecting toughness

One of the main original aims of brittle-matrix composites research has been to increase the work of fracture, and hence toughness, of brittle materials. Unfortunately, factors which lead to the greatest increase in ultimate strength do not necessarily yield optimum increases in the work of fracture.

The work of fracture may be defined as the work done per unit area in propagating a crack.

Experimentally, the energy required to fracture a test-piece in a controlled, non-catastrophic manner is found by integration of the region bounded by a load–deflection curve, and this is subsequently divided by twice the cross-sectional area of the specimen [8,40]; thus, surface irregularities produced during crack propagation are usually neglected. This technique measures the mean fracture energy for the total process. In general, the crack initiation energy is not equal to the energy required to propagate a crack, but may be greater in the case of a brittle ceramic, or less in the case of a ductile-metal or fibre-reinforced ceramic. It is possible to measure the fracture initiation energy by a suitable fracture-mechanics analysis [41], but when crack propagation is more difficult than initiation, the work of fracture technique yields a more realistic engineering parameter.

One mechanism by which the total work of fracture may be raised is to increase the effective crack propagation area by providing planes of weakness within the material, in a direction parallel to the tensile axis, along which a propagating crack may be deflected [42]. For the case of a unidirectionally aligned fibre composite, a propagating crack may be deflected along a weak interface and hence the crack tip is blunted. Progressive delamination of the specimen may follow, particularly during flexural deformation, and Aveston [39] has shown that high values for the work of fracture are possible by this mechanism. However, due to the requirement of very weak interfaces such a material would not be expected to be particularly strong; however, since this mechanism does rely on weak interfaces it is independent of the mechanical properties of the fibre employed.

If the fibre–matrix interface is sufficiently strong a crack may propagate relatively unimpeded through the composite. Some work is required to debond fibres in the immediate vicinity of the crack plane [43], but this is a relatively small contribution. If continuous brittle fibres are employed, the fibres will usually fracture in the primary crack plane and this will not contribute very significantly to the total work of fracture, although this increases with fibre diameter [44]. However, if discontinuous fibres are employed of length  $l < l_c$ , the fibres will not be loaded to their fracture stress and must be withdrawn from the matrix as the fracture planes separate. It has been

shown [45] that the contribution due to pull-out can be very significant, and the maximum value,  $\gamma_{p_{\max}}$ , is obtained for  $l = l_c$ , when:

$$\gamma_{p_{\max}} = \frac{V_f \tau l_c^2}{12r} \quad (7)$$

where  $\tau$  is the interfacial shear-stress resisting pull-out. If the fibre length  $l > l_c$ , pull-out is still observed since some fibres will intersect the crack plane within a distance  $l_c/2$ , and hence a fraction  $l_c/l$  of fibres will not be loaded to their fracture stress, and must pull-out as the planes separate. The contribution,  $\gamma_p$ , due to pull-out will be less than for the optimum case, and can be given by [32]:

$$\gamma_p = \left(\frac{l_c}{l}\right) \frac{V_f \tau l^2}{12r} \quad (8)$$

Since  $l_c = \sigma_f r / \tau$ , where  $\sigma_f$  is the fibre fracture stress, the contribution due to pull-out, for a given system, can usually be estimated. The fact that pull-out effects have been observed for certain continuous brittle-fibre systems has been attributed to the statistical distribution of strength along such fibres allowing fracture of many fibres to occur at positions away from the fracture plane [44].

The requisites of a strong interface for strength and a relatively weak interface for toughness may sometimes be combined by employing a duplex fibre element. This may consist of a cylindrical outer sheath, which is strongly bonded to the matrix surrounding an inner core element which is less strongly bonded to the sheath. When failure of the outer sheath occurs, pull-out effects are obtained between the sheath and inner element [46, 47].

If discontinuous ductile fibres are employed, high values for work of fracture may also be obtained by the pull-out mechanism. However, a large contribution is also possible by plastic flow and rupture of fibres. For fibres of length  $l > l_c$ , the contribution,  $\gamma_r$  due to fibre rupture will be:

$$\gamma_r = V_f \gamma_f (1 - l_c/l) \quad (9)$$

where  $\gamma_f$  is the fibre rupture energy. Unfortunately, the high work of fracture of metals cannot always be fully utilized due to wire embrittlement which

may occur during fabrication [48].

Further, the thermo-mechanical history of the metal reinforcement may be important in determining the failure mode of a composite. Thus, it has been observed for a model resin-metal wire system, that work-hardened wires fracture when the embedded length exceeds a critical length, whilst annealed wires invariably pull-out of the matrix, regardless of the embedded length [49]. Apparently this effect is due to the plastic reduction in cross-sectional area of the wire propagating towards the embedded end of the wire, hence reducing the frictional bond strength, until the wire is able to pull-out. It is possible that if long ( $l > l_c$ ) annealed wires of very high work-hardening capacity were employed, the strength of bridging fibres might increase sufficiently during limited plastic deformation to allow pull-out of the majority of the embedded fibre length, rather than continued plastic deformation; possibly such a mechanism could increase the work of fracture above that which would be obtained by fibre rupture alone, or pull-out of shorter lengths, although this has not been attempted in practice.

If fibres are randomly oriented, many fibres will cross the fracture plane obliquely and will be subject to a bending moment. For the case of brittle fibres this will lower the applied tensile stress required to fracture the fibres, but with ductile fibres, plastic bending may accommodate the extra strain at the convex portion of the fibres during withdrawal from the matrix, and may contribute significantly to the total work of fracture. If fibres make a small enough angle to the fracture plane they will be unable to pull-out, at least initially, and will either fail in shear, or will break through the matrix. It has been shown that the maximum work of fracture due to pull-out of aligned ductile fibres of critical length is significantly greater than that which can be obtained by plastic bending alone of misaligned fibres. However, the deformation of misaligned fibres can make a substantial contribution to the work of fracture when fibres of less than the critical length are employed, and which would not yield very high values when aligned [48, 50]. Unfortunately, with randomly-oriented reinforcement, some fibres will lie approximately perpendicular to the tensile axis and may act as stress-concentration sites, particularly if bonding is weak, consequently reducing the strength of the composite.

### 2.2.3. Summary of major factors contributing to composite strength and toughness

#### 2.2.3.1. Brittle-fibre systems.

(1) For optimum strength and stiffness continuous fibres, or discontinuous fibres of length  $l \gg l_c$ , should be employed, and the difference in moduli and strengths should be as large as possible. Fibres should be unidirectionally aligned parallel to the tensile axis to prevent the occurrence of shear deformations or bending moments which would reduce the effective tensile strength of fibres. Since  $l_c$  depends on the interfacial shear stress, a strong chemical or frictional bond is desirable. Additional strengthening can be obtained when  $\Delta\alpha$  is negative if a strong fibre-matrix bond exists, but positive  $\Delta\alpha$ , or negative  $\Delta\alpha$  in the absence of bonding, may lead to a reduction in strength.

(2) For optimum toughness, however, fibre pull-out is essential and aligned discontinuous reinforcement of length equal to the critical length should ideally be employed. Weak interfaces can be utilized to promote delamination effects.

(3) Hence, a compromise between strength and toughness is necessary. This may be accomplished by utilizing fibres of length  $l > l_c$ , or by using continuous fibres which exhibit a large statistical distribution of strength along their lengths to allow some pull-out effects. Alternatively, either continuous fibres in the form of impregnated bundles of large effective diameter or duplex fibres, may sometimes be employed.

#### 2.2.3.2. Ductile-fibre systems.

(1) For optimum strength the same conditions hold as for the brittle-fibre case, but fibre yield-strength rather than tensile strength should be as high as possible, and the effect of misalignment is not as detrimental.

(2) The conditions for optimum toughness are more open to compromise. Hence, although high work of fracture values can be obtained with pull-out effects, high toughness can also be obtained by fibre rupture, due to expenditure of energy in plastic deformation. Also, relatively high toughness may be obtained using short or weakly bonded fibres due to shear and plastic bending contributions from fibres crossing the crack plane obliquely, although in this instance the composite strength will be significantly lower than that of the aligned system.



#### *2.2.4. Other factors influencing mechanical properties*

With many ceramics the initial flaw size remains relatively unchanged until the fracture stress is reached. Others, however, exhibit a phenomenon known as sub-critical crack growth [51], in which cracks slowly extend during application of a given stress until they reach a critical size at which propagation becomes catastrophic. A typical example is glass in a water-containing environment [52], and the phenomenon is generally referred to as "static-fatigue". In some respects this may be related to the familiar stress-corrosion susceptibility of certain metals in corrosive environments [53], and can lead to time-dependent catastrophic failure in components which are stressed at levels well below their normal yield or fracture stress. It may be expected that the presence of particles or fibres may increase the resistance of a ceramic to static-fatigue by interfering with crack growth during the initial stage, but this is not well documented.

The effects of dynamic fatigue in ceramics or glasses are also not well documented. Fatigue in metals is attributed to a dislocation mechanism and it is not observed during cyclic stressing in the elastic region [54]. Hence, it would be expected that materials which do not exhibit plastic flow would not be subject to dynamic fatigue. However, cases have been reported for fibre-strengthened glasses [55], in which the normal fracture stress is reduced and the fracture mode shifted from controlled to semi-catastrophic after cyclic straining at levels well below the normal failure stress, and this has very important implications if such materials are to be used for components which may be subject to cyclic stresses. It is possible that such an effect is related to static fatigue or to differential elastic modulus effects, but more work is required on this extremely important subject.

#### *2.2.5. Factors affecting mechanical properties at elevated temperatures*

Factors affecting strength and toughness at elevated temperatures are less well documented and are not clearly understood. Thermal stability and long-term compatibility become a major factor if a component is to be used for prolonged periods at elevated temperatures, and hence a system which exhibits good properties at ambient temperatures may become non-viable at elevated temperatures, due to fibre degradation. Many systems are in-

compatible at elevated temperatures due to direct reaction between the component phases. The thermo-chemical compatibility of various fibre-reinforced ceramics has been reviewed by Krochmal [56] with particular reference to their equilibrium diagrams.

Thermal stability of the reinforcement is also of importance for continued service conditions. Metal wires may become annealed during high-temperature service, and the resulting decrease in yield strength may adversely affect the composite strength and creep resistance. The most appropriate method of combating this, whilst retaining the advantages of metal reinforcement, would be to use certain precipitation-hardened alloys, such as Nimonic alloy wires, or even dispersion-strengthened metals, such as TD-Nickel, which retain very high yield strengths at elevated temperatures.

The effect of static fatigue may become more pronounced at elevated temperatures due to enhanced chemical reactivity. However, for ceramics, a stage will be reached when dislocation mobility becomes high enough to allow some plastic relaxation at crack tips, and hence the presence of cracks becomes of less importance at elevated temperatures. In general, polycrystalline ceramics exhibit increasing strength with decreasing grain size at ambient temperatures, but the converse may be true at elevated temperatures due to effects such as grain-boundary sliding and diffusional creep [9]. Grain-boundary sliding may be particularly predominant in glass-ceramics due to viscous flow of the thin intercrystalline glass layer. The presence of fibres may be expected to decrease the time-dependent deformation of ceramic materials if the fibres themselves have adequate creep resistance, and are bonded to the matrix. Stable, adequately bonded particles or fibres may also minimize grain-boundary sliding by exerting an additional pinning effect on the boundaries. As dislocation mobility increases at elevated temperatures, dynamic fatigue may also be expected to become important and a fine particle dispersion should be most effective in inhibiting this.

The resistance of a material to thermal shock is also of paramount importance for components such as turbine blades or rocket nozzle-inserts which may experience extremely rapid temperature fluctuations during service [57]. The higher the thermal expansion of a material the higher the stresses experienced during thermal shock

conditions. Hence, for ceramics in which high stresses cannot be accommodated by plastic flow, the resistance to thermal shock is very low. The only real answer would be to use ceramics of very low expansion, such as certain glass-ceramics, but the limitation in other properties may not allow this. However, the resistance to thermal shock can be increased by addition of high-conductivity fibres which help to redistribute the stresses more evenly; fibres may also hold the body intact in the event of matrix failure.

Finally, the elevated temperature properties may also be affected by variation of such parameters as  $\Delta E$  or  $\Delta\alpha$  with temperature, which may lead to changes in the magnitude of internal stresses [58]. The variation of thermal expansion with temperature for various matrix and reinforcement materials is illustrated in Fig. 1.

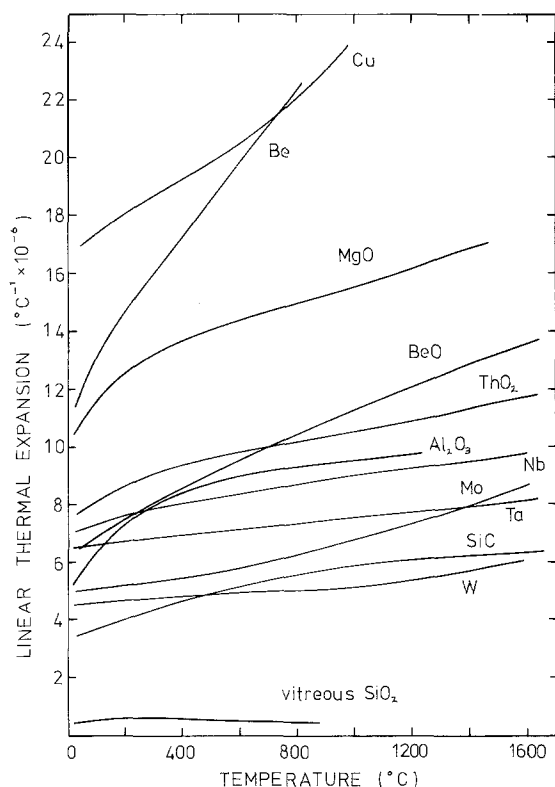


Figure 1 Variation of linear thermal expansion coefficient with temperature for various matrix and reinforcement materials (from tabulated data [141]).

### 3. Experimental systems

#### 3.1. Dispersion-strengthened glasses and ceramics

By suitable choice of alloying additions and heat-treatment, many glasses and ceramics may be strengthened by precipitation of a secondary

phase. For instance, certain glasses may be induced to undergo phase separation to produce amorphous-amorphous systems, or may be partially crystallized to form amorphous-crystalline composites. The latter phenomenon has given rise to glass-ceramics [59], but these may only be regarded as dispersion-strengthened glasses when the volume fraction of crystalline phase is relatively low since practical glass-ceramics may approach 100% crystallinity. Unfortunately, although generally stronger than the homogeneous glass, these materials still exhibit catastrophic failure and correspondingly low values for work of fracture.

Similarly, certain polycrystalline ceramics [60–64] and some single crystal ceramics including MgO [65–67], Al<sub>2</sub>O<sub>3</sub> [68] and NaCl [69], have been successfully precipitation-strengthened. The MgO–Al<sub>2</sub>O<sub>3</sub> binary system [70] is a classical example of a precipitation-hardenable “alloy” which exhibits decreasing solubility of one component in another with decreasing temperature. Unfortunately, the fracture toughness of these materials is still extremely low and these systems are of little practical value as engineering materials.

Dispersion-strengthened glasses and ceramics have also been prepared by standard powder metallurgy techniques, and may be broadly classified according to  $\Delta\alpha$ . If the value is large and positive, the resultant internal stresses after cooling from the fabrication temperature may be sufficient to promote microcracking of the matrix, and such an effect has been reported for several systems.

For instance, Frey and Mackenzie [71] observed microcracking in a glass–Al<sub>2</sub>O<sub>3</sub> composite of  $\Delta\alpha = +6.9$  and similar effects have been reported for BeO–SiC with  $\Delta\alpha = 2.3$  [72]. Tummala and Friedberg [73] observed weakening of a glass–ZrO<sub>2</sub> system with  $\Delta\alpha = +4.4$  but they did not actually indicate if the system was microcracked. Rossi [74] also observed microcracking of a MgO–W system for volume fractions of tungsten greater than about 3%. Substitution of the appropriate values into Equation 1, indicates that the matrix fracture stress is expected to be exceeded, and hence a microcracked system is anticipated in the cases cited.

Rankin *et al.* [75] observed slight weakening of an Al<sub>2</sub>O<sub>3</sub>–Mo system of positive  $\Delta\alpha$ , but grain size, controlled by the fabrication conditions, was found to be the main factor controlling the

materials strength; the relatively coarse ( $\sim 50\mu\text{m}$ ) dispersion apparently did not inhibit grain growth. However, McHugh *et al.* [76] observed significant strengthening of an  $\text{Al}_2\text{O}_3$ -Mo system when sub-micron molybdenum powder was employed, and this they did attribute to the fine dispersion directly limiting the grain size of the matrix. Carnahan [77], however, noticed weakening of an  $\text{MgO}$ -W system in spite of the fact that the fine particles inhibited grain growth, but in this instance the value of  $\Delta\alpha$  is significantly higher than that of the  $\text{Al}_2\text{O}_3$ -Mo system, and hence the internal stresses are greater.

When  $\Delta\alpha$  approaches zero, or exhibits small negative values, the matrix is no longer in tangential tension, and significant strengthening has been observed for systems in this category. Tummala *et al.* [73] observed strengthening for a glass-ZrO<sub>2</sub> system of  $\Delta\alpha = -2.9$  but only when "rounded" particles were employed; angular particles produced weakening which they attributed to stress-concentration effects. Similarly, Fray *et al.* [71] observed strengthening of glass- $\text{Al}_2\text{O}_3$  and glass-ZrO<sub>2</sub> systems exhibiting negative  $\Delta\alpha$  values, and Nivas and Fulrath [19] observed strengthening of a glass-tungsten system of near zero  $\Delta\alpha$ . However, if the negative value of  $\Delta\alpha$  is too large the particle-matrix interface may be unable to withstand the induced radial tensile stresses and the resultant decohesion may leave voids. This has been observed for glass-nickel systems of  $\Delta\alpha \sim -12$ , for particle sizes greater than  $10\mu\text{m}$ , by Hasselman, and Bertolotti and Fulrath [18, 78]. However, it was found that when oxidized nickel powder was employed, strengthening did occur, presumably due to the higher interfacial bond strength. Weakening has also been observed for an  $\text{Si}_3\text{N}_4$ -SiC system of negative  $\Delta\alpha$  [79]. The normalized strength as a function of dispersoid concentration is illustrated for various typical systems in Fig. 2.

In all instances where work of fracture measurements have been performed, marginal increases have been reported, but the systems still remain brittle, and liable to catastrophic failure [48, 67, 75, 79].

It is interesting to note that the melt viscosity of certain ceramics is phenomenally increased by particle additions. For instance, Dunn [80] found that an  $\text{SiO}_2$ -20 vol%W system possessed such a high viscosity, even at  $2300^\circ\text{C}$ , that the specimen did not flow to fill the crucible, although

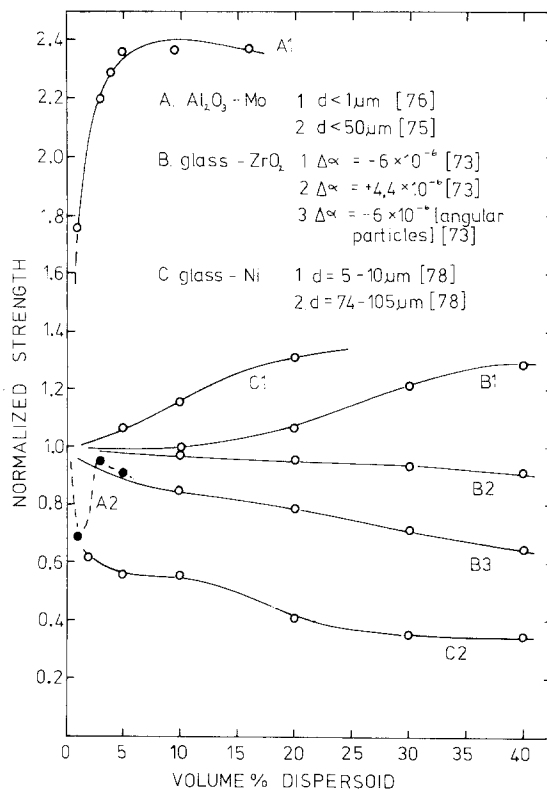


Figure 2 Variation of normalized composite strength with dispersoid volume fraction for experimental systems.

the softening point of  $\text{SiO}_2$  had been exceeded by about  $650^\circ\text{C}$ . Similar effects have been observed for certain metallic-matrix systems including  $\text{Ag-Al}_2\text{O}_3$  [81, 82], and  $\text{Al-Al}_2\text{O}_3$  [83] and it is possible that surface tension forces between the metal and ceramic are strong enough to prevent the flow normally associated with a liquid.

### 3.2. Fibre-reinforced glasses and ceramics

A significant amount of work has been carried out during the last few years on fibre-reinforced cements and these materials are of very practical value in the civil engineering field. Cements offer great potential for fibre strengthening due to their low modulus, and it has been shown that significant strengthening and increased work of fracture may readily be achieved by utilizing a variety of reinforcements, including metal wires, glass fibres, asbestos and carbon fibres, and  $\text{Al}_2\text{O}_3$  fibres [84-89]; the validity of Equation 3 has been confirmed in many cases [32]. Also, polymer impregnation has been utilized in conjunction with fibre reinforcement with very pronounced effects [90]. As summarized in Section 2.2.1, the scope with other brittle matrices is more limited,

but nevertheless many relatively successful systems have been reported. These may be classified into brittle-fibre or ductile-fibre systems, and may be sub-divided according to  $\Delta\alpha$ . A summary of the fabrication techniques which have been employed in the production of these materials is presented first.

### 3.2.1. Fabrication techniques

The most widespread technique for the fabrication of fibre-reinforced ceramics and glasses is hot-pressing. Randomly oriented fibre systems are prepared by tumbling, high-speed blending, or simply mechanically shaking fibre/matrix-powder mixtures, followed by loading into a suitable die and pressing at elevated temperature, usually in vacuo or inert atmosphere; densities approaching 100% of theoretical can readily be achieved by this process. It is desirable to employ matrices of higher thermal expansion than that of the die material, unless hot-ejection facilities are available, otherwise difficulty is experienced in removing the sample when cool, and if the differential is sufficiently large, cracking of the die body may occur prior to compact removal. Chemical compatibility is a further serious problem at elevated temperatures. Graphite dies are often employed due to the ease of machining this material, coupled with its low thermal expansion and chemical inertness; pressing must be carried out in an inert atmosphere because of the very poor oxidation resistance of graphite, and die and punches have to be changed fairly frequently owing to its poor abrasion resistance. Graphite also exhibits low strength and impact resistance, although it is relatively inexpensive. Dies fabricated from stronger and more abrasion-resistant materials including Mo-Ti-Zr (TZM) alloy [91,92], stainless steel [93], and silicon carbide [91] have been employed but exhibit various disadvantages. For instance, stainless steel is characterized by a very high thermal expansion coefficient whilst inert liners must usually be employed with TZM alloy.

During hot-pressing some alignment of fibres generally occurs so that they tend to lie in the pressing plane, but within this plane they are randomly oriented. Unidirectionally aligned fibre systems have been prepared by several techniques including passing continuous fibres through a slip of matrix powder and binder [93], and extruding discontinuous fibre-matrix powder slips containing ammonium alginate into an acid fixing

bath which yields a tape of aligned fibres [94]. In both instances the tapes may be cut into desired lengths or shapes and hot-pressed after a suitable heat-treatment to remove the binder. Unfortunately, hot-pressing demands relatively expensive equipment, and it is time-consuming; hence, it is of limited commercial value.

Cold-pressing followed by sintering has been utilized [93,95-97], but although this is generally a quick and simple operation, materials of relatively low percentage theoretical density are often obtained, and severe compact warpage may occur during shrinkage. Since porosity can have pronounced deleterious effects on the mechanical properties of ceramics and glasses this technique has not been widely employed. Slip-casting has also been utilized [98], but this method similarly yields materials of high residual porosity.

Plasma-spraying has been reported for the production of  $\text{Al}_2\text{O}_3$ -Mo, and  $\text{Al}_2\text{O}_3$ -W systems [99], but this cannot be seriously considered as a commercial production technique. Casting has been utilized to prepare certain glass- $\text{Al}_2\text{O}_3$  fibre systems [100]; however, the melt viscosity was found to increase significantly and hence casting became more difficult as the volume fraction of fibre was raised; difficulty was also experienced in adequately mixing the fibres into the melt. Extrusion techniques have also been employed for preparing certain aligned glass-crystal compositions [101], and ceramic-metal systems [102], and this technique may offer considerable scope for preparation of other aligned systems.

Finally, various unidirectionally solidified ceramic-metal eutectic structures have been reported. Galasso *et al.* [103] prepared a unidirectionally solidified  $\text{BaFe}_{12}\text{O}_{19}$ - $\text{BaFe}_2\text{O}_4$  system containing aligned plates of the second phase. Johnson and Benjel [104] reported unidirectional solidification of  $\text{HfO}_2$ -W systems, but noted that successful fibre structures were only obtained for low tungsten concentrations. Similarly, Watson *et al.* [105], experienced difficulty in controlling the structure of  $\text{ZrO}_2$ -W systems. Chapman *et al.* [106], were able to produce a  $\text{UO}_2$ -W system by a modified floating-zone process, and noted that regular eutectic structures were produced in spite of the fact that the entropy of melting of  $\text{UO}_2$  is considerably greater than that of tungsten. Clausen [107] successfully prepared  $\text{Gd}_2\text{O}_3/\text{GeO}_2$ -Mo, and  $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ -Cr structures by unidirectional solidification but noted that cavities

were formed in the rod centre; to overcome this problem he comminuted the rods and hot-pressed the resulting powder to yield randomly oriented fibre structures. Chapman *et al.* [108] have reported several other melt-grown ceramic-metal composite systems. Although it is possible by the unidirectional eutectic solidification technique to produce well-bonded aligned systems with fibre diameters down to a few micrometres or less, the technique is limited to specific systems and full control of the process is extremely difficult; various types of eutectic structure may be formed in a given system, and this is often coupled with extensive void formation. Hence, at the present time, this technique would appear non-viable for serious commercial applications.

### 3.2.2. Mechanical properties

**3.2.2.1. Brittle-fibre systems.** The most successful systems, in terms of low and intermediate temperature properties, are found in this category. For instance, several unidirectionally aligned carbon-fibre and graphite-fibre systems have been reported to exhibit ambient temperature strengths approaching  $900 \text{ MN m}^{-2}$  and values for work of

fracture of the order of  $10^4 \text{ J m}^{-2}$  [93,109]. However, when randomly oriented discontinuous reinforcement is employed a decrease in strength is often observed, although work of fracture is still significantly greater than that of the unreinforced matrix. For instance, Sambell *et al.* [110] observed a decrease in strength of 50% for a 20 vol% fibre-borosilicate glass system, although work of fracture was increased from 4 to  $350 \text{ J m}^{-2}$ . The decrease in strength was found to be even more pronounced for  $\text{Al}_2\text{O}_3$ , and particularly MgO systems which exhibit large positive  $\Delta\alpha$  values and the MgO system was found to be micro-cracked after fabrication. An  $\text{Al}_2\text{O}_3$  system containing graphite or silicon carbide fibres has been reported to yield marginal improvements in work of fracture, but mullite fibres were found to react with the matrix at the fabrication temperature [111]. Several systems have been reported, however, in which randomly oriented fibres have significantly strengthened a given material, the classical example being the cement composites [84-90]. Kliman [100], also observed strengthening of glass- $\text{Al}_2\text{O}_3$  fibre systems of zero  $\Delta\alpha$  prepared by casting, and special porcelain- $\text{Al}_2\text{O}_3$

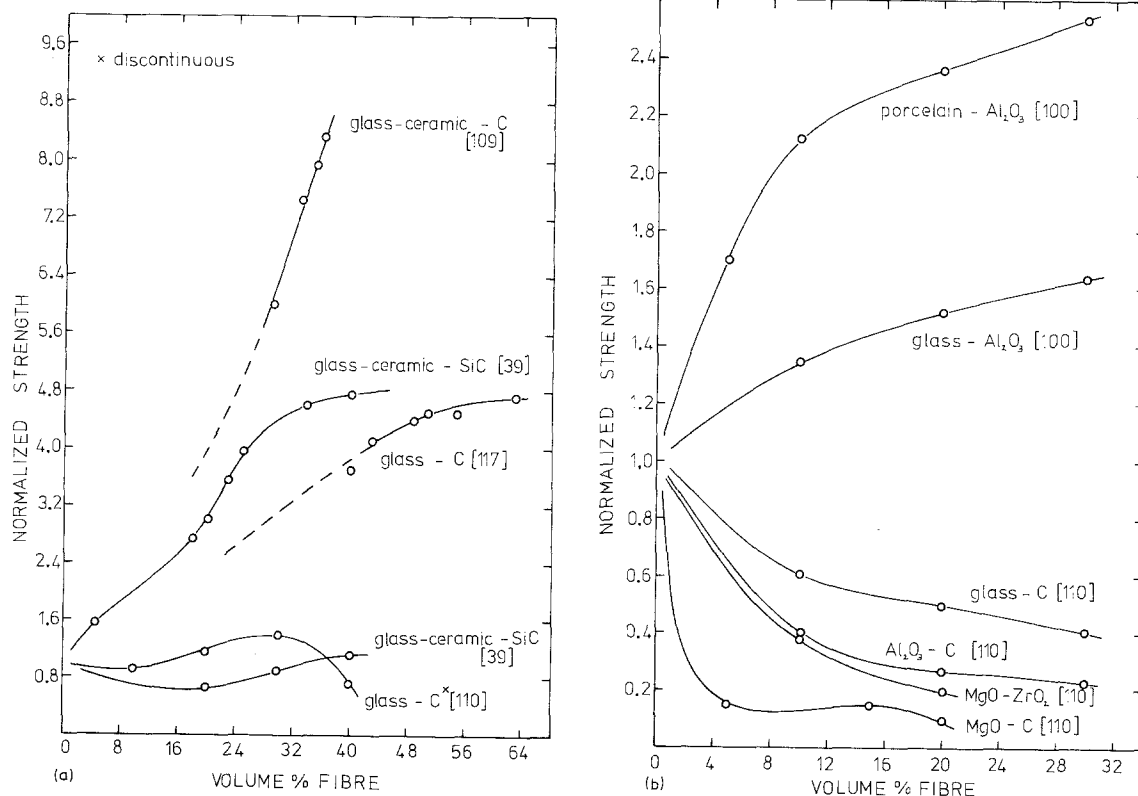


Figure 3 Variation of normalized composite strength with fibre volume fraction for (a) aligned, and (b) randomly oriented, brittle-fibre systems.

fibre compositions for fibre volume fractions less than about 40%.

Pre-stressed composite systems which exhibit negative  $\Delta\alpha$  have also been successfully prepared. Aveston [39] reported glass-ceramic unidirectionally aligned silicon carbide-fibre systems which exhibited strengths approaching  $700 \text{ MN m}^{-2}$ , and values for work of fracture of the order of  $2 \times 10^4 \text{ J m}^{-2}$ . The strengthening was attributed to the fibre pre-stressing the matrix in compression on cooling from the fabrication temperature, but this only occurred under certain fabrication conditions which yielded strong matrix-fibre bonding. Lindley and Godfrey [112] have also reported pre-stressed  $\text{Si}_3\text{N}_4$ -SiC fibre systems with moderately improved strength and toughness. The variation of strength with fibre volume fraction is illustrated in Figs. 3a and b for aligned and randomly oriented experimental systems.

Although the aligned carbon-fibre reinforced systems are quite impressive with respect to strength and toughness at ambient temperatures, unfortunately, at the present time, they are of little practical value for elevated temperature applications in oxidizing environments. This is due to the fact that carbon is readily oxidized in air at temperatures greater than about  $400^\circ\text{C}$ , and protection of the fibres by the matrix is usually very limited due either to matrix porosity or to progressive matrix microcracking during service, which may occur at levels appreciably less than the ultimate failure strength of the composite. Systems which are already microcracked exhibit catastrophic decreases in strength at temperatures above  $400^\circ\text{C}$  [110]. It has, however, been shown that the high strength of continuous carbon-fibre-glass-ceramic systems is maintained at temperatures up to at least  $800^\circ\text{C}$  in non-oxidizing atmospheres [93], but such conditions impose severe restrictions for their general use. Limited work has been carried out on coating carbon-fibres with an oxidation-resistant material in an attempt to overcome this difficulty whilst retaining the desirable properties of carbon fibres. For instance, coating with  $2 \mu\text{m}$  thick layers of  $\text{Nb}_2\text{C}$  and  $\text{Ta}_2\text{C}$  has been reported [113], but there are no data available for the performance of such coated fibres in an actual composite system.

Similarly, the pre-stressed systems are limited to service temperatures well below their fabrication temperature due to a loss in the pre-stressing,

and hence ultimate strength, with temperature. Further, not only would the cost of silicon carbide-fibre systems be prohibitively high at the present time, but it has also been shown that silicon carbide-fibres prepared by the standard technique of vapour deposition onto a tungsten substrate are prone to severe thermal degradation at temperatures as low as  $850^\circ\text{C}$  [114].

*3.2.2.2. Ductile-fibre systems.* The increase in strength associated with metal filament reinforced glasses and ceramics is generally far less impressive if compared to that of the aligned carbon-fibre or silicon carbide-fibre systems, but relatively high values for work of fracture have been reported, even for randomly oriented fibres. For instance, Hing and Groves [48] reported a value of  $6.0 \times 10^3 \text{ J m}^{-2}$  for a randomly oriented MgO-33 vol% nickel-wire system, and Simpson and Wasylyshyn [115] obtained a value of  $5.3 \times 10^3 \text{ J m}^{-2}$  for a 12 vol% molybdenum fibre- $\text{Al}_2\text{O}_3$  system; the authors have also obtained values as high as  $3.2 \times 10^3 \text{ J m}^{-2}$  for a glass-ceramic-12 vol% nickel-wire system [116]. These values are considerably higher than those obtained for random carbon-fibre systems and are of the same order as those obtained for continuous aligned systems of high fibre volume fractions, usually in excess of 40 vol% [117]. Impact resistance is also generally improved, and that of  $\text{Si}_3\text{N}_4$  has been found to be significantly increased by additions of tantalum wire [118].

As with brittle-fibre systems, discontinuously randomly oriented ductile reinforcement generally leads to a decrease in strength, and similarly this decrease is greatest for microcracked systems which exhibit high positive  $\Delta\alpha$  values. Hence,  $\text{Al}_2\text{O}_3$ -Mo [95-97],  $\text{ThO}_2$ -Mo [119], and  $\text{ZrO}_2$ -Mo [97] have been found to yield microcracked systems of relatively low strength. In general, systems which exhibit negative  $\Delta\alpha$  values do not yield pre-stressed systems due to inadequate bonding. A possible exception is an  $\text{SiO}_2$ -W system reported by Dungan and Gilbert [92, 120] in which 30 vol% of randomly oriented wire increased the strength almost six times over that of the unreinforced matrix. Einmahl [121] also observed an increase in strength when random dispersions of tungsten-wire were added to a glass of lower thermal expansion, and a maximum strength increase of 270% was observed for a 15 vol% fibre system. He also investigated glass-nickel systems and

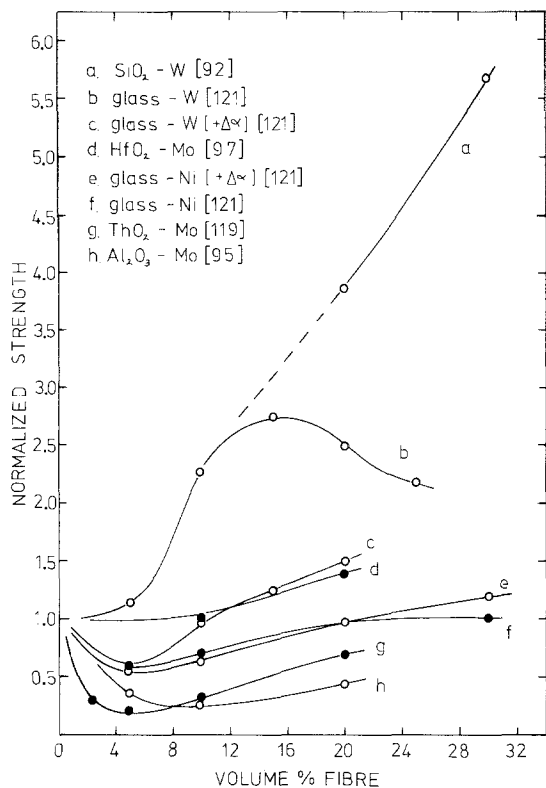


Figure 4 Variation of normalized composite strength with fibre volume fraction for randomly oriented ductile-fibre systems.

found that weakening occurred for nickel volume fractions less than about 25%, independent of  $\Delta\alpha$ , whilst marginal increases in strength occurred for volume fractions greater than 25%. Randomly oriented Mo-wire has also been found to improve marginally the strength of  $\text{HfO}_2$  [97], and mullite [96,122]. Experimental results for ductile-fibre systems are illustrated in Fig. 4.

The high values for work of fracture obtained for randomly oriented ductile-fibre systems are probably related to the work required to deform the fibres plastically; misaligned brittle fibres break at reduced stresses, hence contributing little extra work. Experimental systems are compared in Fig. 5. The thermal shock resistance of metal-wire reinforced systems is generally significantly improved in that the composite may retain a relatively high proportion of its strength after a thermal shock which would disintegrate the unreinforced matrix [95-97]. However, the matrix generally undergoes a process of extensive microcracking which may be deleterious to the long-term elevated temperature stability of the system. Unfortunately, very little work has been

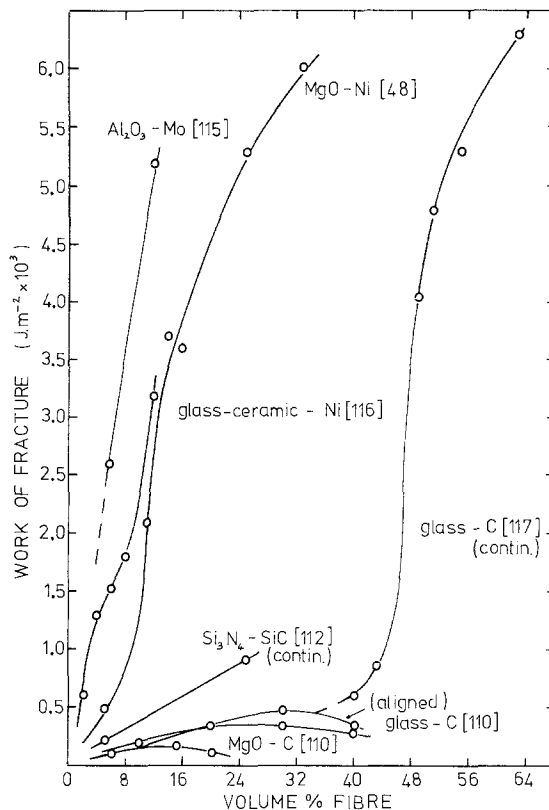


Figure 5 Variation of work of fracture with fibre volume fraction for experimental systems.

carried out on general elevated temperature properties; however, it has been observed that severe oxidation of tungsten and molybdenum wires occurs for microcracked systems in air at temperatures above about  $700^\circ\text{C}$  [95-97] and this would rule out the use of such reinforcement for general elevated temperature use, particularly if subject to thermal shock. It has been reported [123] that the thermal stability of  $\text{UO}_2\text{-ThO}_2$  fuel elements has been improved by the incorporation of molybdenum fibres although niobium fibres were found to be unsatisfactory due to chemical reaction with the matrix.

Finally, metal honeycombs, rather than fibres, of platinum and inconel have been used to reinforce  $\text{ThO}_2$  and  $\text{MgO}$  [124], and other reinforcement configurations including grids [125], and wools [98] have been utilized, with some success.

3.2.2.3. Prediction of mechanical properties at ambient temperatures. A comparison between experimental and theoretical strengths for various systems is given in Table II. The value of

TABLE II Comparison between experimental and theoretical strength of various discontinuous randomly oriented fibre systems

System	Reference	$V_f$	$\Delta\alpha$ ( $\times 10^{-6} \text{ }^\circ\text{C}^{-1}$ )	Experimental flexural strength		Upper-bound	Lower-bound
				Absolute ( $\text{MN m}^{-2}$ )	Normalized	experimental	experimental
MgO–Carbon fibre	[110]	0.05	+13.5	30	0.15	7.43	6.50
	[110]	0.20	+13.5	20	0.10	14.50	8.90
Borosilicate glass –carbon fibre	[110]	0.20	+3.5	58	0.61	3.55	2.05
$\text{Al}_2\text{O}_3$ –carbon fibre	[110]	0.20	+8.8	81	0.27	4.57	3.23
MgO– $\text{ZrO}_2$ fibre	[110]	0.10	+5.9	76	0.38	2.89	2.42
	[110]	0.20	+5.9	40	0.20	6.00	4.20
$\text{Al}_2\text{O}_3$ –Mo fibre	[95]	0.05	+2.8	92	0.37	2.99	2.63
	[95]	0.10	+2.8	67	0.27	4.46	3.48
	[95]	0.20	+2.8	113	0.45	3.07	1.90
$\text{Al}_2\text{O}_3$ –Mo fibre	[115]	0.06	+2.7	135	~1.0	1.27	0.96
	[115]	0.12	+2.7	135	~1.0	1.53	0.91
$\text{Al}_2\text{O}_3$ –Mo fibre	[96]	0.20	+2.8	158	0.67	2.13	1.28
	[97]	0.10	+0.2	72	1.03	1.89	0.88
$\text{HfO}_2$ –Mo fibre	[97]	0.20	+0.2	98	1.36	2.06	0.58
	[119]	0.10	+3.6	35	0.33	4.83	2.94
$\text{ThO}_2$ –Mo fibre	[119]	0.20	+3.6	76	0.71	3.05	1.33
	[122]	0.20	–0.4	161	1.95	1.32	0.49
SiO <sub>2</sub> –W fibre	[92]	0.20	–4.3	186	3.86	1.41	0.30
	[92]	0.30	–4.3	276	5.71	1.33	0.21
Mullite–W fibre	[122]	0.20	+0.6	157	1.89	1.84	0.52
Glass–W fibre	[121]	0.10	+3.5	68	1.02	2.53	1.12
	[121]	0.15	+3.5	83	1.24	2.70	0.98
	[121]	0.20	+3.5	101	1.50	2.73	0.85
	[121]	0.25	+3.5	57	0.86	5.77	1.60
Glass–W fibre	[121]	0.05	–0.9	66	1.15	1.67	0.92
	[121]	0.10	–0.9	131	2.30	1.24	0.50
	[121]	0.15	–0.9	157	2.75	1.38	0.44
	[121]	0.20	–0.9	142	2.50	1.89	0.51
Glass–Ni fibre	[121]	0.10	+3.5	47	0.66	1.77	1.55
	[121]	0.20	+3.5	64	0.91	1.47	1.19
	[121]	0.30	+3.5	73	1.02	1.45	1.07
	[121]	0.40	+3.5	92	1.44	1.27	0.88
Glass–Ni fibre	[121]	0.05	–6.3	41	0.61	1.80	1.68
	[121]	0.10	–6.3	47	0.70	1.70	1.49
	[121]	0.20	–6.3	66	0.98	1.39	1.11
	[121]	0.30	–6.3	73	1.08	1.41	1.03
	[121]	0.40	–6.3	92	1.37	1.25	0.84
	[121]	0.50	–6.3	112	1.67	1.13	0.71
Glass-ceramic –Ni fibre	[116]	0.02	–8.3	78	0.35	2.85	2.85
	[116]	0.08	–8.3	76	0.34	2.89	2.89
	[116]	0.12	–8.3	85	0.38	2.58	2.58
	[116]	0.08	+1.7	131	0.63	1.57	1.57



$\Delta\alpha$  is taken for cooling from the fabrication temperature to room temperature. The rule of mixtures upper value was determined from Equation 2a; however, since the failure strain of the matrix is less than that of the fibre for brittle-matrix composites, matrix cracking is usually observed prior to ultimate failure, and hence  $\sigma'_m$  has been replaced by  $\sigma_{um}$ . The lower value was obtained using Equation 2b, with the value of  $\sigma'_f$  obtained from the relationship,  $\sigma'_f = E_f \sigma_{um}/E_m$ . An efficiency factor was employed for randomly oriented fibre systems; this was taken as  $\frac{1}{3}$  since, in general, orientation is random in two dimensions for hot-pressed systems. A corresponding efficiency factor for fibre length was not employed due to the uncertainty in the value of  $l_c$  for any given system; hence, in effect, it was assumed that  $l \gg l_c$  for all systems, so that the values reported for discontinuous reinforcement must be regarded as an upper limit. Further, even for continuous fibre systems accurate theoretical estimates are again made difficult due to the uncertainty of fibre strength. The "as-received" fibre strength is generally not reported in experimental results, and further it is usually not known to what degree mechanical or thermal degradation of the fibre may have occurred during fabrication. The mean values in Table I are generally used in determining the strengths, unless the "as-received" fibre strength was reported in the appropriate paper; hence, in general, this will further raise the estimate of composite strength. The statistical variation of strength along fibre length is generally also unknown and may be expected to modify the composite properties again, particularly work of fracture. Finally, it should be noted that, strictly speaking, the theoretical equations apply to tensile strengths and the experimental values reported are invariably flexural strength obtained in three-point, or occasionally four-point bending. Since the exact relationship between tensile and flexural strength depends on the appropriate value of the Weibull modulus for that system [126] it is not appropriate universally to predict tensile strength from flexural strength, and for brittle materials flexural strength may generally be two to three times greater than tensile strength. Hence, it is usual to employ the appropriate matrix flexural strength value in the equations in order to estimate the corresponding flexural strength of the composites, although the fibre tensile strength is usually employed; however,

during flexural deformation in a composite, the fibres are also subjected to a bending moment which may significantly reduce their effective strength, and hence again lead to an over estimation of theoretical strength.

If the ratio of theoretical to experimental strength is plotted against  $\Delta\alpha$  for discontinuous fibre systems a broad parabola is approximated centred slightly to the negative side of the  $\Delta\alpha$  axis. For the upper theoretical value the apex lies approximately within the range, 0.9 to  $2.0 \times \sigma_t/\sigma_e$ , whilst for the lower value it lies within 0.1 to 0.9. Hence, as  $\Delta\alpha$  increases for either positive or negative values, the ratio of theoretical to experimental strength also increases; as expected, the upper limit usually predicts too high a value for composite strength. As  $\Delta\alpha$  becomes more negative, it is likely that if fibre-matrix bonding does exist at the fabrication temperature, decohesion will occur on cooling, and stress transmission to the fibres will depend on a frictional bond which itself will become weaker as  $\Delta\alpha$  becomes more negative, and hence the ratio of theoretical to experimental strength is expected to increase. Conversely, when  $\Delta\alpha$  is positive, the matrix is strained in tension, and hence the matrix contribution to composite strength is expected to decrease. This will yield a system in which matrix cracking will begin at a strain lower than the normal cracking strain of the unreinforced matrix, and in the limit the matrix will be microcracked initially after fabrication and the matrix contribution will then be zero. However, if the matrix strain is taken into account, by modifying Equation 2 to:  $\sigma_c = \frac{1}{3} \sigma_{fu} V_f + (\epsilon_m - \epsilon'_m) V_m$ , the ratio of upper theoretical strength to experimental strength is usually still too high, even for continuous fibre systems. A further factor to be considered is that, in the case of positive  $\Delta\alpha$ , the fibre will be in compression, and since this would tend to increase the ratio still further, it must be assumed that significant fibre damage does occur during fabrication. The weakening of many randomly oriented systems at relatively low volume fractions of fibre, is probably explained on the basis of stress-concentration effects. Hence, fibres oriented out of the tensile axis will act in a similar manner to Griffith flaws, thus reducing the applied stress required to initiate failure of the matrix. Fig. 6a and b illustrate that, in general, for randomly oriented systems, if  $\Delta\alpha$  lies within the approx. range  $-7$  to  $+14 \times 10^{-6}$  the composite

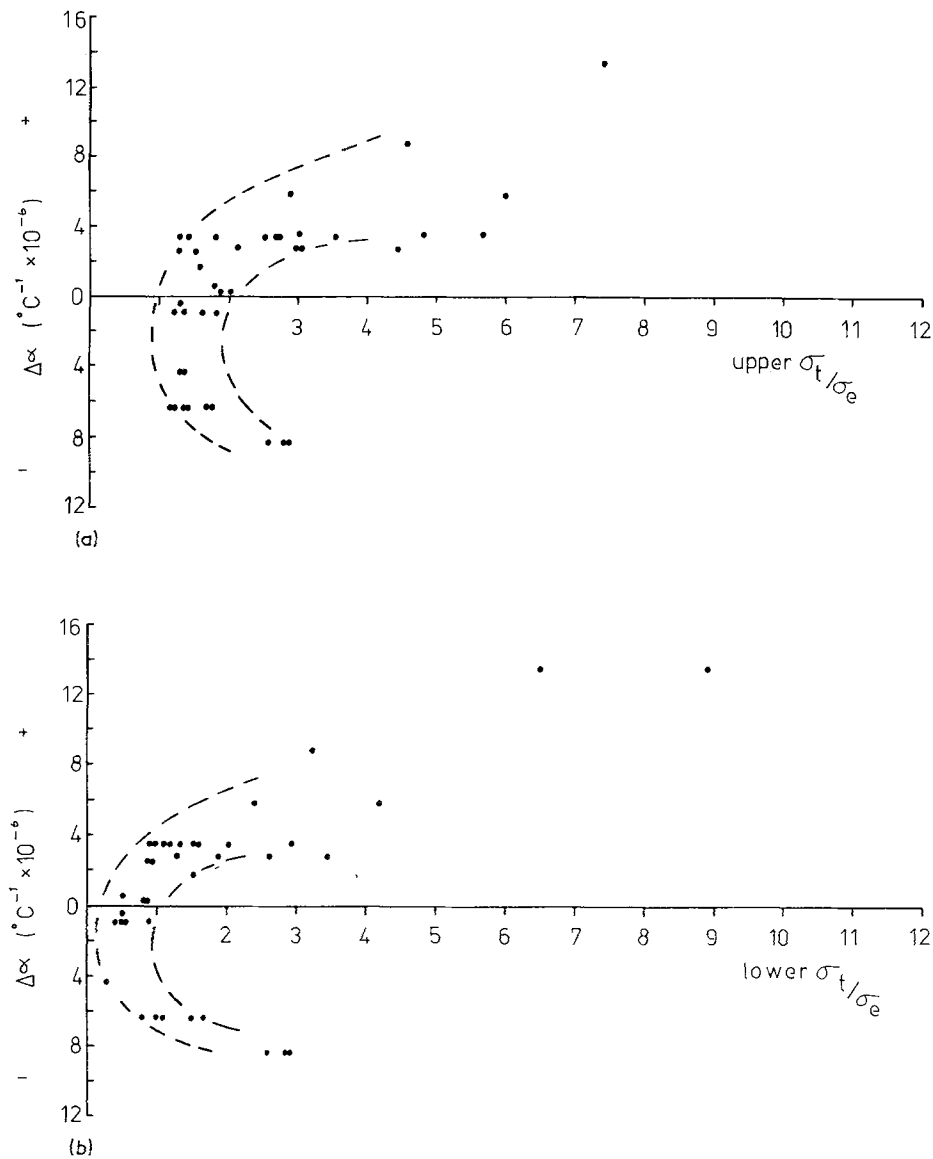


Figure 6 Variation of  $\Delta\alpha$  with (a) the ratio of the upper-bound theoretical to experimental strength, and (b) the ratio of the lower-bound theoretical to experimental strength. (see text, Section 3.2.2.3.)

strength falls within the upper and lower bounds set by the rule of mixtures, as defined by Equations 2a and b. If, however,  $\Delta\alpha$  lies outside this range the lower bound also predicts too high a value for composite strength.

There are not enough data available on work of fracture measurement to speculate on the variation of work of fracture with  $\Delta\alpha$ . It would be expected that for brittle-fibre systems work of fracture would be greatest for weak interfaces, and Phillips [127] has observed such a variation with two continuous carbon-fibre systems, although taken

in general there seems to be no well-pronounced trend, as illustrated in Fig. 7. Reference to Fig. 7 does, however, illustrate the general superiority of ductile-fibre systems, in terms of toughness.

#### 4. Potential applications

At the present time, fibre-reinforced glasses and ceramics have not provided viable alternatives to more conventional metallic materials, and much more work is required if such materials are ever to become acceptable replacements. However, their range of potential applications is extremely

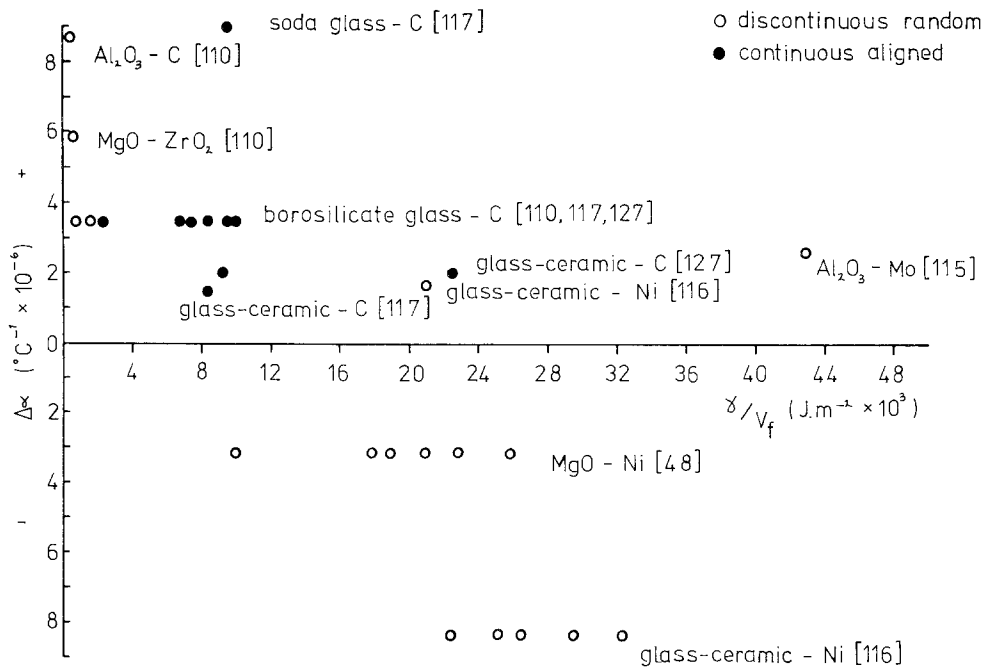


Figure 7 Variation of  $\Delta\alpha$  with the ratio of the work of fracture to fibre volume fraction for experimental systems.

diverse and hence the incentive for further investigation is high, as summarized below.

#### 4.1. High-temperature materials

The strength to weight ratio as a function of temperature for metallic alloys and ceramics is compared in Fig. 8a and b respectively, from which it can be seen that many ceramics retain a high proportion of their strength at temperatures well in excess of  $1200^{\circ}\text{C}$ , and hence might be expected to provide useful high-temperature materials. From the early days of the gas turbine a considerable amount of work has been directed toward the production of better materials for turbine components, particularly compressor and turbine blades. The maximum operating temperature, and hence efficiency and performance, of a gas turbine is limited by the materials available [128], although notable effort has been directed toward cooling technology [129]. Conventional Nimonic alloys are limited to maximum operating temperatures around  $1000^{\circ}\text{C}$  for continuous service, whereas ceramics such as silicon nitride or silicon carbide may be used to at least  $1200^{\circ}\text{C}$ , or even higher, if problems associated with the poor creep resistance, low toughness, and susceptibility to sub-critical crack growth can be overcome [126], and fibre reinforcement offers a promising method

of accomplishing this. The low density, and hence high strength to weight ratio, coupled with the high oxidation resistance of many ceramics also makes them ideal candidates for general high-temperature aerospace applications such as thermal protection shrouds, leading-edges, and rocket nozzle inserts; the requirements of materials for missile and space-craft applications have been reviewed by Steinberg [130]. Unfortunately, although fibre-reinforcement generally enhances the resistance of a ceramic to thermal shock, fibre composites often show a tendency toward matrix microcracking under conditions such as thermal shock or stressing at levels below the ultimate composite strength, and the problems associated with a microcracked system during extended service have not been fully investigated. The effects of dynamic fatigue may also be important, particularly at elevated temperatures, and more work is required to evaluate the response of candidate materials to such service conditions. The long-term thermal stability of the system is also of importance for extended service, as outlined earlier, and finally, the response of such materials to mechanical impact also warrants further detailed investigation. In all instances, the variation of properties with specimen size and shape is also of paramount importance, partic-

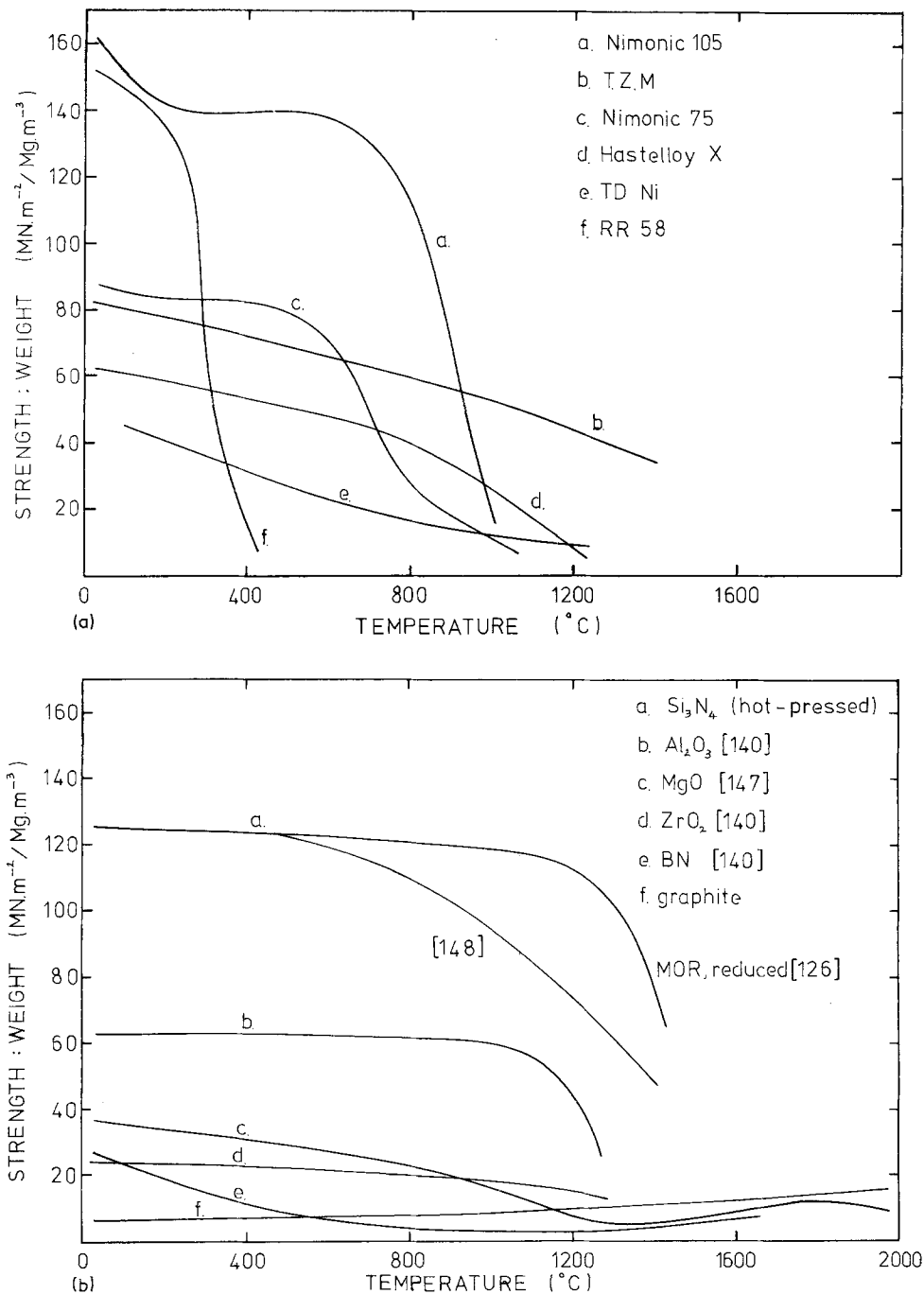


Figure 8 Variation of the tensile strength to weight ratio with temperature for (a) metallic alloys, and (b) ceramics (tensile strengths taken from commercial data unless reference quoted).

ularly in view of the infamous failure of carbon-fibre reinforced compressor blades once used in the RB211 engine.

#### 4.2. Ballistic-protection materials

Conventional steel armour plating used in military applications for tanks and armoured personnel

carriers imposes a severe weight penalty which limits vehicle manoeuvrability, transportability and general performance, whilst light-weight vehicles based on aluminium, although more manoeuvrable, may lack adequate ballistic protection [131]. Similarly, protection of space-capsules against micro-meteorite bombardment

necessitates the use of ultra light-weight materials due to rocket pay-load limitations. It is known that certain ceramics backed up by a metallic support plate are effective armour materials due to their high elastic modulus, which may prevent ballistic penetration by causing disintegration of the projectile. However, ballistic impact may cause extensive damage to the plating over a relatively wide area due to the extreme brittleness of the armour, and hence the protection offered may decrease catastrophically, even at distances far removed from the initial impact. It is possible that the ballistic efficiency of such materials may be significantly improved if the low density and hardness of suitable ceramics could be combined with adequate toughness and spalling resistance by fibre reinforcement. Although some work has been reported on ceramic-metal laminate armour plating [132–135] the majority of work is classified.

### 4.3. Biomedical materials

The excellent corrosion resistance of many ceramics may offer a more desirable alternative to the metallic-base materials including stainless steels, titanium, Co:Cr, and Co:Cr:Mo:Ni alloys conventionally used for such applications as bone support pins and hip prostheses. Since metals are not inert to the biological environment many cases of severe inflammation or necrosis of tissue have been reported due to the toxicity or irritability of gradually dissolving implants [136–139]. Metals are also susceptible to stress-corrosion failure in such environments and cases have been cited where catastrophic failure of hip prostheses has occurred [137]. It is possible that suitable inert ceramics, when toughened by fibre reinforcement, may offer a new class of superior biomedical materials, and the carbon-fibre systems may excel in such applications.

## 5. Conclusions

(1) Significant particle strengthening may be obtained only if the following conditions are satisfied:

(i) the elastic modulus of the particles is greater than that of the matrix, although there are exceptions when grain-growth inhibition may be important;

(ii) stress-concentration effects due to adverse particle shape are minimal;

(iii) if  $\Delta\alpha$  is positive particle size should be

small (i.e. sub-micron), and strengthening will be mainly attributable to grain-growth inhibition; however, if the value of  $\Delta\alpha$  is too high, or if high volume fractions are employed, induced tangential tensile stresses will weaken the matrix, and in the limit microcracking will occur which can be predicted using Selsing's formula;

(iv) if  $\Delta\alpha$  is negative strengthening may occur if strong particle-matrix bonding exists, but if the interface cannot support the induced stresses on cooling voids will be initiated and weakening will result.

(2) The maximum strength attainable by particle reinforcement is generally only two to three-times that of the unreinforced matrix.

(3) Maximum increases in work of fracture may be obtained for particle reinforcement if the fracture toughness of the dispersed phase is greater than that of the matrix, and strong bonding exists; but any mechanism by which crack deflection may be obtained can marginally improve work of fracture; however, in all instances the increase is less than an order of magnitude and hence of questionable significance.

(4) Suitable fibre reinforcement can provide large increases in strength approaching an order of magnitude, and increases in work of fracture may approach three or four orders of magnitude.

(5) Continuous brittle-fibre systems (i.e. carbon and silicon carbide fibres) have provided the most successful composites, in terms of strength and toughness at ambient temperatures, but they are of little practical value for extended elevated temperature use.

(6) For high work of fracture values with brittle fibres, pull-out effects are essential, but rupture of ductile fibres can lead to high work of fracture without the necessity for pull-out.

(7) Randomly oriented fibres generally produce weakening, although there are notable exceptions; brittle fibres yield only small increments in work of fracture whilst ductile fibres can provide large increments.

(8) The strength of a given fibre composite cannot be accurately predicted by the rule of mixtures criteria even if the state of matrix strain, due to expansion mismatch, is taken into account; this is due to the uncertainty of the *in situ* value of fibre strength, and in the case of discontinuous reinforcement to the value of the fibre critical length, and the effect of misaligned fibres as stress-concentration sites.

(9) The ratio of theoretical to experimental strength increases with  $\pm \Delta\alpha$  for randomly oriented systems. In general, if  $\Delta\alpha$  lies within the range  $-7$  to  $+4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  the composite strength falls within the lower and upper theoretical bounds as defined in the text, whilst if  $\Delta\alpha$  lies outside this range, the lower bound also predicts too high a value for composite strength.

(10) Fibre reinforcement, particularly with ductile fibres, generally improves the resistance of a ceramic to thermal shock, but matrix micro-cracking may be initiated.

(11) The potential of fibre-reinforced ceramics is high, but only if several important aspects, as outlined below depending on the potential use, are fully evaluated, can they seriously be considered as useful structural materials:

- (i) dynamic and static fatigue resistance;
- (ii) impact resistance
- (iii) thermal shock and thermal fatigue resistance;
- (iv) long-term thermal stability
- (v) the effect of progressive matrix micro-cracking on these properties, and the effect of the environmental conditions and specimen size and shape.

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