PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Composites for the 1990s [and Discussion]

A. Kelly, F. E. Buresch and R. H. Biddulph

Phil. Trans. R. Soc. Lond. A 1987 **322**, 409-423
doi: 10.1098/rsta.1987.0060

Phil. Trans. R. Soc. Lond. A **322**, 409–423 (1987)
Printed in Great Britain

Composites for the 1990s

By A. Kelly, F.R.S.
Vice-Chancellor's Office, University of Surrey, Guildford, Surrey GU2 5XH, U.K.

Composites are of two essentially different types: (*a*) those made to achieve a unique combination of properties, usually mechanical properties; (*b*) composites formed for ease of processing. The archetype of (*a*) is the fibre or laminated composite. The attainable properties will be reviewed and interesting effects arising from the scale of size of the components discussed, notably crack arrest and thin-film effects. Examples of (*b*) are polymer–polymer composites and some of the processes for forming ceramics and strong metals. A unified example of (*a*) and (*b*) are composites of controlled thermal conductivity.

1. Introduction

There are many composite materials used in engineering that are *not* designated as such, for example the WC–Co cutting tool, the car tyre, the plain bearing (Al–Sn or CuSn–Pb–PTFE), particulate magnets; many superconductors consist of aligned superconducting wires (for example Nb_3Sn) in a copper matrix. The term composite is usually used of *fibrous composites*, for example, a polyester resin reinforced with glass fibres to make a corrosion resistant pipe. *Advanced* composites means stiff fibres, for example, of graphite, aramid (based on polyparabenzamide) B, SiC, Al_2O_3 or stiff glass in a low-density matrix of resin for new constructional materials used in transportation.

The interest in fibre composites by a sophisticated industry (aerospace) has demanded the growth of a relatively small body of new science that relates the colligative properties of fibrous composites to the properties of the individual components; for equiaxed composites this was not a vital necessity. There have not been many surprises, for example large nonlinear synergistic effects, but some interesting mechanical effects are observed, for example a negative thermal expansion and Poisson ratio and interesting combinations of properties have been obtained not hitherto obtainable in a single material, for example a magnetoelectric device better than the best single-phase transducer and an extremely bright fluorescent screen for X-rays by combining a good secondary electron emitter and a good scintillator (anthracene). The most striking combination is that of high strength and stiffness coupled with resistance to fracture and low density.

The conventional description of composites describes them as multicomponent materials designed to achieve a combination of physical properties. I believe that there is another type of composite emerging, which in some cases may include the first type, and that is the composite formed for ease of processing of a material. This is a composite where a second material (B) is added to a first (A) so that the first can be manipulated into the desired physical form. The B-component may or may not then be removed. Examples would be the use of a processing aid in the production of macrodefect-free cement (see, for example, Birchall 1983) and the use of a processing control agent in mechanical alloying (see, for example, Gilman & Benjamin 1983). The recently described process leading to what are called 'lanxide' composite materials,

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

and the use of polymethylmethacrylate to make a castable substitute for sanitary ware are other examples. These are processes that I believe will become of great importance in the 1990s.

2. HIGH-PERFORMANCE FIBRE COMPOSITES

The properties of the types of fibre available today are shown in figures 1 and 2. Of course, the fibres must be dispersed within a matrix and to reduce the anisotropy, laminated structures are used. Some comparison of the mechanical properties attainable compared with competitor (aerospace) materials are shown in figure 3. The advantages over conventional materials then become much more modest after lamination. There is also a counter attack occurring from the metal industry: Al–Li alloys now pose something of a threat to graphite epoxy composites.

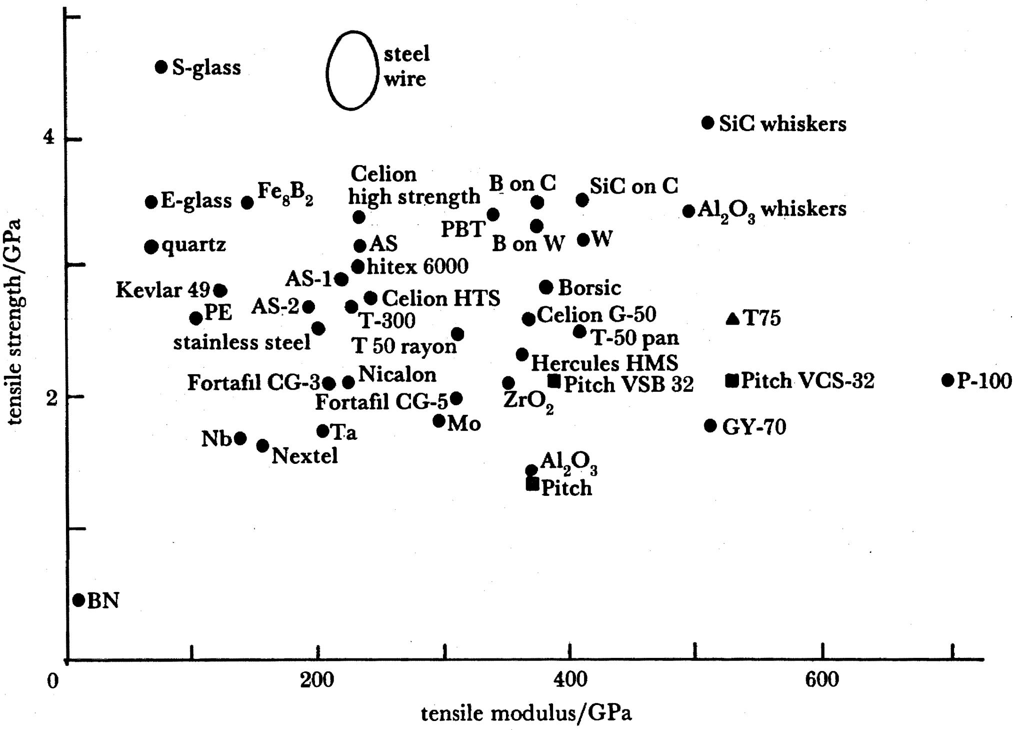

FIGURE 1. Tensile strengths and stiffness of a variety of fibres.

Over a range of components, Pope (1985) quotes that, where 40% of an aluminium-alloy structure is replaced by carbon-fibre-reinforced plastic (CFRP), savings of 12% of total mass can be expected; additional benefits then accrue from the resulting reduction in mass of the aircraft itself. These advantages coupled with the high resistance to fatigue of CFRP mean that CFRP is well worth developing. There are problems with electromagnetic compatibility because the electrical conductivity of CFRP is much lower than that of aluminium alloys. In high-stress design, allowance must be made for the non-ductility of CFRP. An additional difficulty is that epoxy resin absorbs moisture over long periods of time.

However, the natural anisotropy once regarded as a disadvantage is now being very imaginatively used to control dynamic and aeroelastic response. Helicopter rotor blades suffer from forced vibrations at particular rotor frequencies. The transmission of undesirable

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

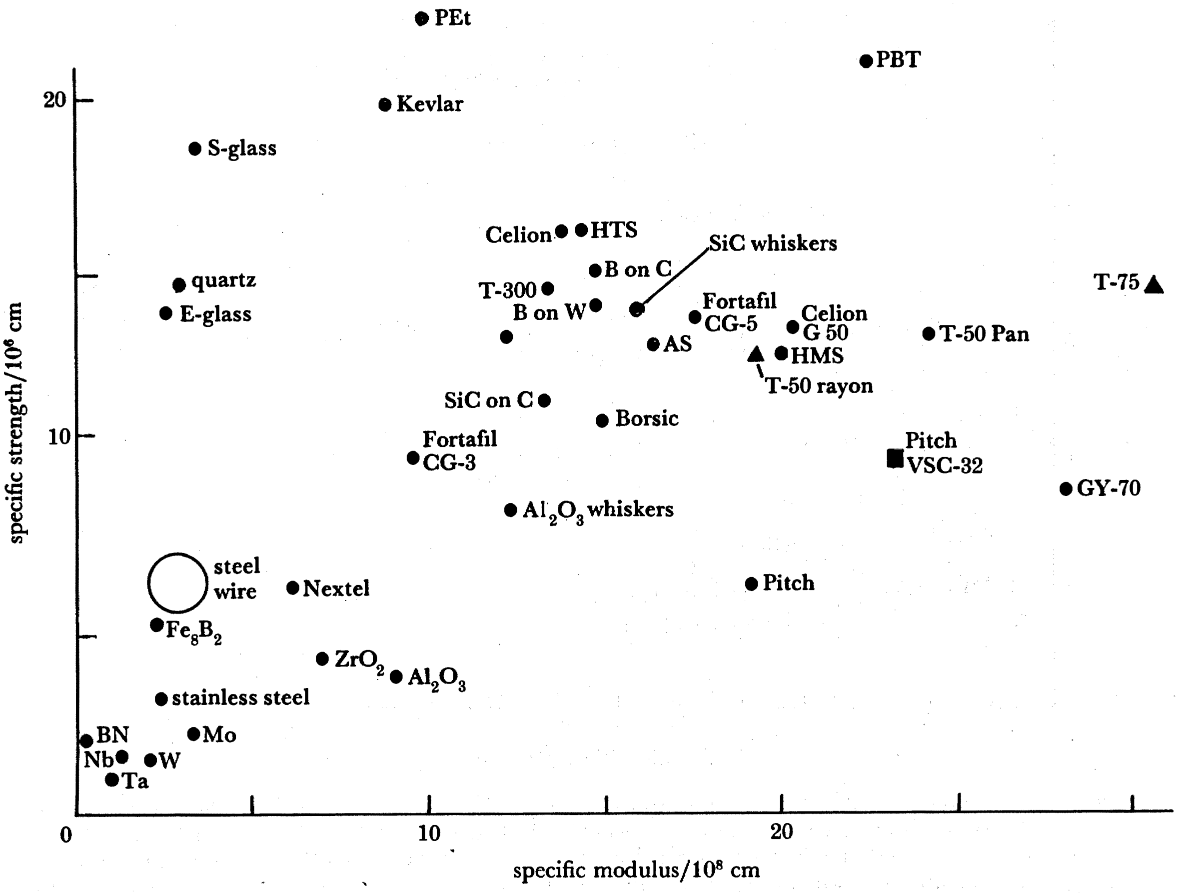

FIGURE 2. Specific strength and stiffness of a variety of fibres. The specific value is the value of the property divided by $g\rho$ where ρ is the density and g the acceleration due to terrestrial gravity.

vibrations to the rest of the structure can be modified by varying the material's stiffness along the blade, which is not feasible with a metal blade. Forward sweep of fixed wings gives advantage for manoeuvrability in the transonic speed range. With conventional materials the forward swept wing becomes very heavy. In composite materials, judicious laminate stacking can be used to increase the resistance to twisting and to bending independently of one another which is not possible with an isotropic material. This aeroelastic tailoring is now being demonstrated in the Grumman X-29 so that forward-swept wings may be introduced.

Aromatic thermoplastic matrices are in principle much better than thermosets having, if crystalline, the advantages of infinite shelf life, resistance to water and to solvents, some ductility and hence reproducible strength and toughness. They are more rapidly processable, better adapted to robotics, and can be joined by welding with advantage of repairability and the possibility of scrap recycling. This, coupled with the advantages of using metal forming machinery, means that we can expect replacement of thermoset by thermoplastic matrices in the 1990s, if the price comes down.

Composite materials of course imply composite structures; the first time the term was used in engineering was in the clipper ships! Al beams with fibrous composite backing (Arall, a composite structure on a miniature scale) also point the way to the future.

Returning to figures 1 and 2, one is struck by the wealth of materials available today

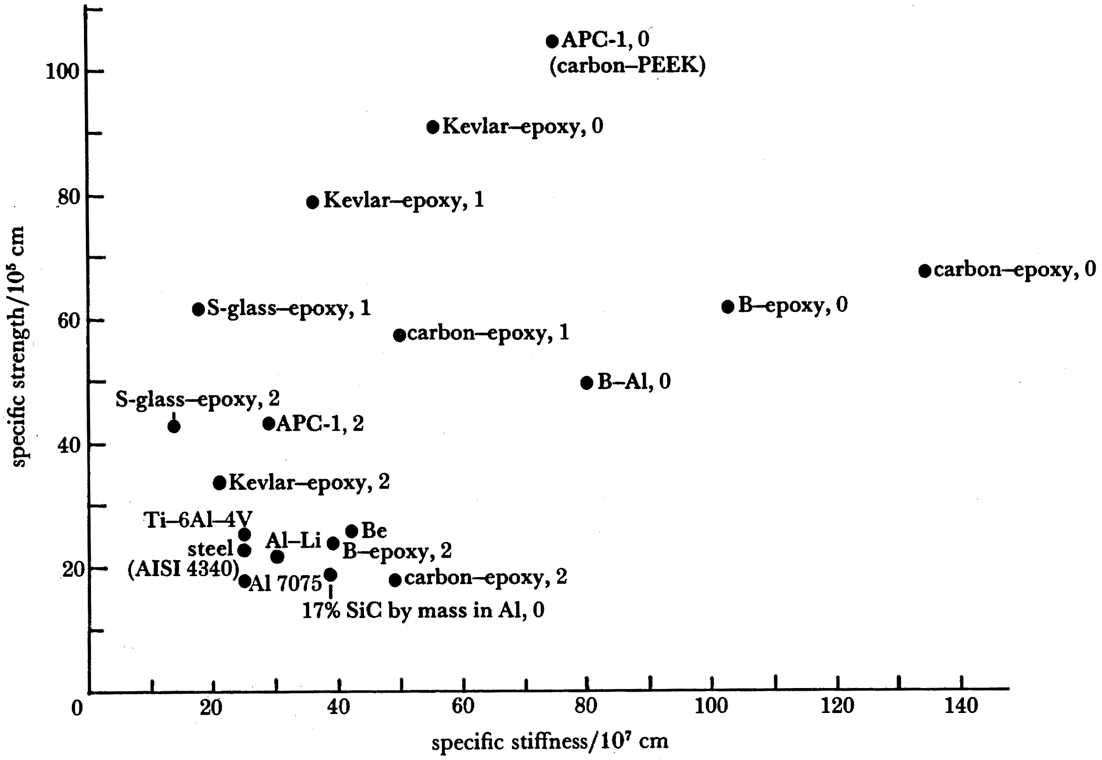

FIGURE 3. Specific strength and stiffness of some isotropic materials and of fibre composites. The designation 1 on the composites means the following arrangements of fibres: 50% at 0°; 40% at ±45° and 10% at 90° to the stress; 2 denotes balanced laminates with equal proportions at 45°, 90° and 135°; 0 indicates aligned fibres in the specified matrix. The volume fraction of fibres in the various composites are not the same in the different systems. They vary between 40 and 60%.

compared with the situation fifteen years ago. The variety of strong and stiff fibres ready to hand means that it is now much easier to select combinations of materials for specific uses where it is necessary to match the properties to those of an existing system or interface. For example, reinforcing polyethylene with hydroxyapatite for a bone replacement (Bonfield *et al.* 1984) or designing materials with specific acoustic impedances.

3. METAL MATRICES AT LOW TEMPERATURE

Metal-matrix composites have recently been reviewed by Chou *et al.* (1985). So far as reinforced fibrous composites for aerospace are concerned, the interest in a metallic matrix centres on the use of lower-density metals and the avoidance of the disadvantages of a matrix based on a thermosetting resin. Epoxy and similar resins possess low thermal conductivity, and a high thermal expansion coefficient. They show dimensional instability, hygrothermal degradation, material loss in high vacua and are susceptible to radiation damage and embrittlement at low temperatures. The lighter metals do not possess these disadvantages.

Many metal matrix systems involving reinforcing fibres have been explored including Be, B, C, silicon carbide and alumina (of various types) fibres in Al as well as B, SiC, Be and W in Ti, and B in Mg. Reinforcement of the light metals Al or Mg is occurring in many cases to reduce wear or reduce creep, for example ICI Saffil in Al alloys. Squeeze casting is often

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

the method of introduction used. The density of Al reinforced with 50–60 vol. % of continuous Al_2O_3 fibres is only some 40% of that of steel but the tensile strength and stiffness in the fibre direction can be the same (table 1.) The fatigue strength in the fibre direction is similar to the value for steel and so such a composite has been produced to make connecting rods in the Toyota experimental FX-1 engine.

When wear, stiffness (as distinct from very high strength), controlled thermal expansion and/or moderate increases in temperature of service are the aim, it is often not necessary to use fibres. Fibres are usually expensive to make compared with other forms of inherently strong solids. By methods based on powder metallurgy very (comparatively) cheap forms of B_4C, SiC and other strong solids can be introduced into aluminium, magnesium and copper matrices. Volume fractions as high as 40% can be obtained and the materials can be forged slowly and welded. Some properties obtained at room temperature taken from the commercial literature are given in table 1.

TABLE 1. PROPERTIES OF PARTICLE- AND FIBRE-REINFORCED METALS

	$\frac{E}{\text{GPa}}$	$\frac{\sigma}{\text{MPa}}$	$\frac{\rho}{\text{Mg m}^{-3}}$	$\frac{E/g\rho}{10^8\text{ cm}}$	$\frac{\sigma/g\rho}{10^6\text{ cm}}$	strain to failure (%)
24 vol. % B_4C in Mg	86	418	1.92 (calc.)	4.4	2.2	0.78
30 vol. % SiC in Al	120	434	2.87	4.2	1.5	3.0
60% (aligned) Al_2O_3 in Al						
longitudinal	262	690	3.45	7.8	2.0	0.3
transverse	152	185	3.45	4.4	0.53	0.6

E, Young's modulus; σ, yield strength; ρ, density

Elastic moduli as high as 208 GPa can be obtained with particles of SiC in aluminium. The mechanical properties of these systems will bear a familial relation to those of the 'hard metals', cf. WC in Co (see for example, Almond 1983). A lot will be learned by application to particulate-reinforced Al alloys of the principles of obtaining toughness, strength and reproducible properties in the hard metals.

4. HIGH-TEMPERATURE METAL MATRICES

Figure 4 shows the 1000 rupture strengths of various materials at elevated temperatures. Composites, particularly directionally solidified fibrous composites, figure prominently. The Nitac and Cotac (not shown) series of alloys are characterized by a very regular distribution of apparently unfaulted fibres. Precipitation and solution strengthening is optimized so as to take full advantage of the fibre strengthening due to 13%, for Nitac 13, of (Ta+V) C fibres (Rabinovitch *et al.* 1983). The γ–$\gamma'Cr_3C_2$ aligned eutectic is included, because although the high-temperature strength is inferior to that of the Nitac and Cotac series, it overcomes two of the major barriers to the commercial exploitation of *in situ* composites, namely extremely stringent processing conditions and relatively (to current superalloys) poor oxidation and corrosion resistance (McLean *et al.* 1982). If directionally solidified fibre eutectics are to become commercially acceptable it will, according to Meetham (1982), be necessary to develop alloys processable under less stringent conditions (as γ–$\gamma'$$Cr_3C_2$ succeeds) and to accommodate the anisotropy of properties.

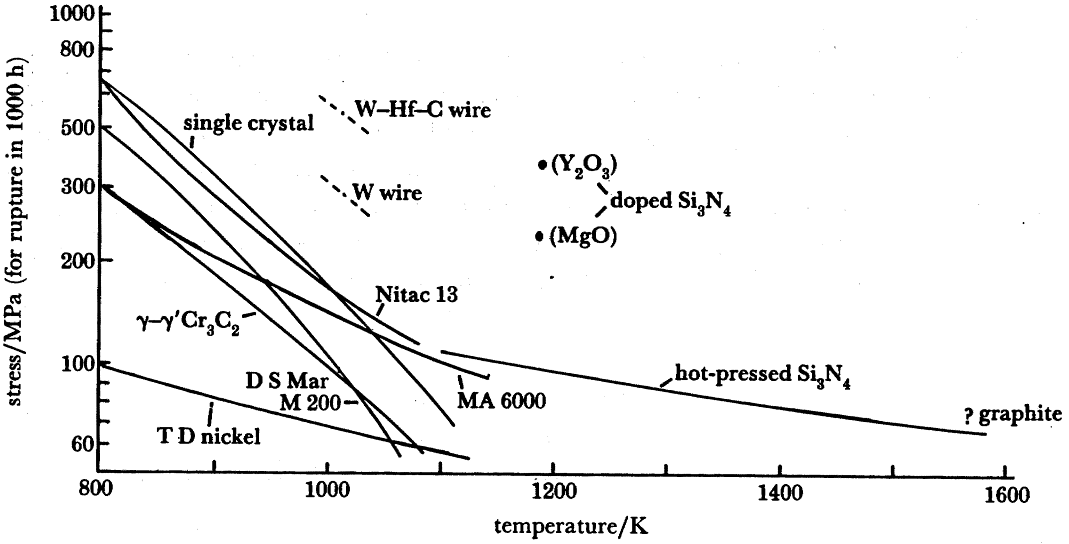

FIGURE 4. 1000 h rupture strength of various materials. For the compositions of the metals and composites see Kelly (1985). The data for doped Si_3N_4 are from Wiederhorn & Tighe (1984).

Figure 4 demonstrates that ceramic materials offer the most promise for extension of service temperature. Graphite at very high temperatures is used as a composite (in reducing atmosphere) as carbon reinforced with carbon fibres. It will be interesting to see whether monolithic ceramics provide adequate properties other than rupture strength; particularly toughness. The ceramic may be carried by a metal in a metal-matrix composite or have toughness provided by the incorporation of fibres.

5. LAMINAR STRUCTURES

There is a rapidly increasing interest in layered microstructures due to (*a*) the production of epitaxial layers of different composition in the microelectronics industry, leading to quantum-well devices (see Phillips, this symposium) and (*b*) because vacuum evaporation is one efficient means of evading ingot metallurgy and the restrictions of alloy composition enforced by the conventional phase diagram. Coevaporation of the main alloy constituents is thermally efficient, (Bickerdike *et al.* 1985) and the method of collection leads directly to a laminated microstructure in a nominally macroscopically homogeneous alloy, (for example 6–9 % Cr–0.6–1.5 % Fe–Al (percentages by mass)) or else a laminated structure is specifically sought by evaporating layers of different composition, for example Al–Ti–Al–Fe. Such layered deposits are not made too slowly, for example 18 kg h^{-1} is attained when working on the 0–100 kg scale.

The high strength of evaporated alloys is derived from the microstructure of the deposits and its further development by working into wrought products. Al–Fe layered microstructures may be heavily rolled and retain the layered microstructure. Within the individual layers there can be a significant contribution to the yield strength from solid solution and dispersion strengthening as well as from dislocation substructure and small grain size: the grain size must be no larger than the layer thickness in one direction and often the grains are equiaxed in three dimensions. With modern techniques uniform layers as thin as one atom diameter may be deposited.

A new type of strengthening, not previously recognized by metallurgists and materials scientists (for example, Brown 1979) arises when the thickness of the layers of, say, two pure metals is reduced below 100 nm or so. This was predicted by Koehler (1970) and satisfactorily confirmed experimentally by Lehoczky (1978).

Suppose a specimen is prepared consisting of alternate layers of pure metals (or other materials) A and B. If the elastic constants differ, dislocations will require a large external stress to drive them from the material of lower elastic constant (say A) into that of higher (B). If the layers are thin enough it may not be possible for a Frank–Read source to operate in either layer and then single dislocations will be the mode of plastic deformation. Lehoczky, following Koehler, finds that the tensile stress in the A layers necessary for penetration of the interface is

$$\sigma_a{}^A = \sigma_m + \sigma_i{}^A, \tag{1}$$

where $\sigma_m = RG_A/8\pi$ and $R = (G_B - G_A)/(G_B + G_A)$ and $\sigma_i{}^A$ is the friction stress in A. The condition that a Frank–Read source operates in A is

$$\sigma_a{}^A = 2\alpha G_A b_A/(\tfrac{1}{2}t_A). \tag{2}$$

In both equations $\sigma_a{}^A$ represents the tensile stress in material A due to an applied stress σ_a on the composite, G is the shear modulus (taken to be C_{44}), b the Burger's vector and t the thickness. Setting $\sigma_i{}^A = 0$, we predict that Koehler strengthening will occur when the right-hand side of (1) is less than the right-hand side of (2) so

$$t \leqslant [32\pi\alpha/R]\, b_A \tag{3}$$

For an Fe–Al layer structure taking $\alpha = 1$, this predicts that Koehler strengthening will occur when the layer thickness of the aluminium is less than *ca.* 47 nm. Actually, Bickerdike *et al.* (1985) find a large increase in *microhardness* of Al–Fe deposits at thicknesses less than about 70 nm.

Accurate tensile tests on foils of Al interspersed with either Cu or Ag have been performed by Lehoczky. In Cu–Al foils containing layers of equal thickness, the tensile yield stress increases inversely as the first power of the layer thickness down to a value of 70 nm and thereafter remains constant at the remarkably high value, for pure metals, of 650 MPa. The ultimate tensile strength (UTS) of such foils is close to 700 MPa; the tensile fracture stress follows a $t^{-\frac{1}{2}}$ relation at thicknesses greater than 70 nm. For Al–Ag foils where the difference in elastic moduli is much less than in Al–Cu (R much smaller) the critical thickness for observation of Koehler strengthening is 230 nm and the strength attained is much less.

The Al–Fe system is very interesting because high hardnesses (and presumably high strengths) are obtained with very small Fe layers, for example, 25 nm of Al and 2% (by mass) (0.7 vol. %) of Fe, which corresponds to 1.7 nm layers. Clearly very high values of strength: mass ratio are possible, for example, a layered structure containing 7.3% (by mass) of iron (2.6 vol. %) has a *tensile strength* (closely equal to the yield strength) of 804 MPa and a specific gravity of 2.82 giving a value of σ/ρ of 285 MPa: 28.5×10^5cm in figure 3, which is high for an Al alloy.

Such high-strength foils show a stress–strain curve in tension rather like that of fibrous composites even though both phases may be pure metals, particularly when the layer thickness becomes very small, for example 20 nm.

The possibilities are intriguing if one considers other possible combinations of layers, for example Al–Ti, Al–Mg, both of which have been successfully made by evaporation. If means other than evaporation are considered, perhaps in concert with it, layer structures of Al–C, Al–SiC, Al–B or Al–AlN (or the same non-metal with Mg) become a possibility. The non-metal would appreciably increase the stiffness, the Koehler effect would strengthen the aluminium, and the resistance to crack propagation in the brittle non metal would be increased by the same effect as occurs in laminates where both phases may be considered brittle, see §6 below.

By direct measurement Lehoczky found an apparent increase in the Young modulus of his Al–Cu foils at thicknesses of the layers of less than about 50 nm. Though the measurements indicate an increased stiffness, whether or not there is a genuine increase in Young's modulus in foils containing thin layers is a very intriguing question at the present time. It has usually been assumed that Young's modulus of a pure pore-free solid cannot be greatly changed except by feeding in energy, for example, in piezoelectric materials. Hilliard and his co-workers at Northwestern University have reported a number of times (see, for example, Baral *et al.* 1985) observing very large increases in the measured stiffness of foils containing layers less than about 3 nm thick. The foils are single crystals and of course account must be taken of the crystalline anisotropy. A very large increase in the Young modulus in the plane of the foil is found in Ag–Pd, Cu–Ni, Au–Ni and Cu–Pd but *not* in Cu–Au (Henein & Hilliard 1983) when there is marked compositional modulation normal to the plane of the foil with a wavelength of 2.0–3.0 nm. The effect disappears at longer wavelengths and at very short ones and is according to these authors very large, for example, by a factor of 2–3. Theoreticians have sought explanations for a genuine increase in the Young modulus in terms of Fermi-surface–Brillouin-zone interactions.

Were the effect found to be real it would be of extreme interest for structural materials, particularly for Al-base layer structures such as Al–Fe mentioned above, because the possibility arises of varying and controlling both strength and stiffness by varying layer thickness. However, I am not yet convinced that a large part of the observed effect is not due to self stress in the foil. When the composition modulation is marked, the interface between the layers rich in one or other of the materials, even if coherent, will have an interfacial free energy of 1 J m^{-2}. Such interfaces spaced 2 nm apart induce in-foil stresses of 0.5 GPa, which are comparable to the stresses applied to the foil in measuring the modulus.

6. BRITTLE MATRICES

Cement containing fibres of asbestos has been known for many years and with glass instead of asbestos for about fifteen (Majumdar 1970). Glass may be replaced, as may asbestos, with cheaper compliant fibres, for example, polypropylene, if the aim is to restrain the material from failing after it has undergone what is called *multiple fracture* (Aveston *et al.* 1971). The engineering principles of fibre cement and concretes are reviewed by Hannant (1978); see also *Bull. Am. Ceram. Soc.* **65** (1986) for work on fibre reinforced ceramics.

There is a growing interest in controlling the onset of cracking in monolithic brittle materials by the addition of fibres for a number of reasons. These are (*a*) ceramics varying from carbon to the high melting point oxides, carbides and nitrides are the *only* materials with temperature capability superior to the nickel alloys (figure 4); (*b*) very-high-strength cements and phosphate-bonded brittle materials are emerging for use at low temperatures that can replace sheet metal in many different applications; (*c*) the addition of fibres to either of these two types of material is a means of imparting toughness and (arguably) provides greater toughness than do other methods, eg. transformation toughening.

The addition of fibres imposes a lower limit on the applied stress (or strain) which must be imposed upon a composite before it can crack. This A.C.K. limit (Aveston *et al.* 1971) has been known for some years but its relation to conventional crack theory and to fracture mechanics has only recently been clarified. I shall follow the approach by McCartney and myself (McCartney 1987), which follows in part the approach of Marshall (1985) but differs importantly in the fracture criterion.

If a brittle material of modulus E_m, plane strain fracture toughness K^m_{Ic}, contains a volume fraction V_f of aligned fibres of circular section, radius r and modulus E_f, a pre-existing crack of length $2a$ within the matrix only, which is spanned by unbroken fibres, cannot run across the specimen unless the strain energy release rate of the composite exceeds $2\gamma_m V_m$, where $2\gamma_m$ is the work of fracture (twice the surface energy in principle for a completely brittle material) of the matrix. It follows that the fracture toughness of the composite for passage of this crack in the matrix alone is

$$K_I = K_{Ic} = [2E_c \gamma_m V_m/(1-\nu^2)]^{\frac{1}{2}} = [V_m E_c/E_m]^{\frac{1}{2}} K^m_{Ic}, \tag{4}$$

where ν is Poisson's ratio.

Provided that we always have σ_∞ (the remote stress on the composite) less than $\sigma_{fu} V_f$, where σ_{fu} is the breaking stress of the fibres (assumed to be constant) then we can model the situation of the fibres crossing the crack and restraining its opening by a non-uniform distribution of pressure on the faces of the crack of opposite sign to σ_∞. Then

$$K_I = \sigma_\infty \surd(\pi a)\, Y, \tag{5}$$

where Y is a function depending upon the elastic properties, volume fraction and radius of the fibres and the sliding friction between fibres and matrix. McCartney (1987) finds values of Y and hence of K_I. By equating K_I to K_{Ic} given by (4) a master curve is produced shown in figure 5, showing the dependence of the critical stress for matrix cracking σ^c_∞ upon the length of a pre-existing matrix crack. The parameters σ_0 and a_0 are related as

$$\sigma_0 \surd(\pi a_0) = K_{Ic} \tag{6}$$

It is seen from figure 5 that there is a limiting stress required to expand even the longest cracks and that the curve is monotonic decreasing, so that if a crack starts to expand it runs all the way across the specimen if the applied stress is maintained. The limit corresponds exactly to the A.C.K. limit. Because for a material without fibres a crack of length $2a$ expands if

$$\sigma^m_\infty = K^m_{Ic}/\surd(\pi a), \tag{7}$$

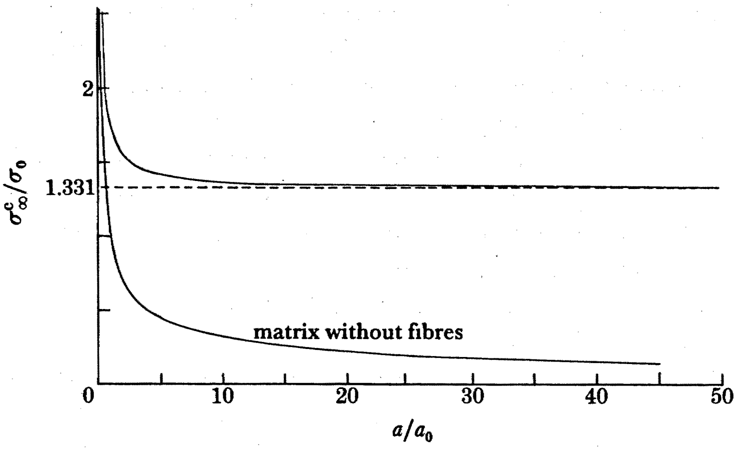

FIGURE 5. The critical stress on the composite for matrix cracking σ^{c}_{∞} as a function of length ($2a$) of the pre-existing crack in the matrix. $\sigma_0 = (\lambda K_{Ic}/\pi)^{\frac{2}{3}}$, $a_0 = (\sqrt{\pi}\, K_{Ic}/\lambda^2)^{\frac{2}{3}}$, $\sigma_0\sqrt{(\pi a_0)} = K_{Ic}$, $K_{Ic} = (V_m E_c/E_m)^{\frac{1}{2}} K^{m}_{Ic}$, $\lambda = (2V_f/V_m)[(2\pi\tau/r)(E_f E_c/E_m^2)]^{\frac{1}{2}}$.

we can, using (4) and (6), express this result as

$$(\sigma^{m}_{\infty}/\sigma_0) = (E_m/V_m E_c)^{\frac{1}{2}}(a/a_0)^{-\frac{1}{2}} \tag{8}$$

with $V_m = 1$ (hence $E_c = E_m$) this represents the curve for the unreinforced matrix. The curve for a matrix without fibres is shown in figure 5. As an illustration, for 7 μm diameter carbon fibres of modulus 234 GPa in a glass with K^{m}_{Ic} of 2 MPa m$^{\frac{1}{2}}$ and $E_m = 58$ GPa, the modulus of the composite, at a volume fraction of 40% fibre is 128 GPa. Values of a_0 and of σ_0 depend on the assumed value of the interphase shear stress τ. If τ is taken as 10 MPa, $\sigma_0 = 535$ MPa and $a_0 = 6$ μm; for $\tau = 60$ MPa, $\sigma_0 = 968$ MPa and $a_0 = 1.8$ μm. Hence if the glass possessed flaws of length ($2a$) of 30 μm, this would correspond to $a = 8.3a_0$ in the latter case and $2.5a_0$ in the former, giving cracking stresses for the material containing fibre, of *ca.* 750 MPa for $a_0 = 6$ μm ($\tau = 10$ MPa) and of *ca.* 1300 MPa for $a_0 = 1.8$ μm ($\tau = 60$ MPa). For the material without fibres the stress for cracking corresponds to complete fracture and is *ca.* 300 MPa from (7). Thus the effect of the fibres is most marked if the matrix contains long cracks so that $a \gg a_0$. A small value of a_0 corresponds to a large value of τ. The presence of the fibres ensures the integrity of the ceramic even after cracking of the matrix and this is perhaps the more beneficial effect than the elevation of the stress for initial cracking of the matrix. The understanding of these effects is giving great impetus to the possible use of ceramics reinforced with fibres in highly stressed situations in the 1990s. The most difficult technical points in the use of these ideas are those of both predicting and measuring a value of the quantity τ and of incorporating the fibres without at the same time introducing excessive or uncontrolled *porosity* into the composite.

7. COMPOSITE PROCESSING

From the definition I gave of composite processing in the introduction, the controlled solidification of eutectics in order to produce a fibrous microstructure would not fall under the definition of composite processing but the formation of polymer–polymer composites, even of block copolymers, would. Takanyagi *et al.* (1980) describe the direct production of a thermoplastic (nylon 6 or nylon 66) containing fibres of polyparaphenylene terephthalamide (kevlar) essentially by copolymerizing and then extruding the sulphuric acid solution of the reaction product into a large amount of water and ethanol. The molecular mass and aspect ratio of the rigid-rod component had a marked effect on the mechanical properties as expected from composite theory. The results have been discussed by Prevorsek (1982) who finds that strengths of the rigid rods in the composite attain 4 GPa; i.e. greater than that of kevlar fibres. I share Prevorsek's view that methods analogous to these in other systems possess great promise if processing speeds can be greatly increased.

Composite processing of the type that I have in mind does not necessarily imply the production of fibrous composites. Ceramics are the ideal strengthening agents for a metal at high temperature. The dispersion of the ceramic particles, principally yttria and some carbides in the alloy MA6000 depicted in figure 4 must be in the size range 0.1–1 μm and at a spacing of the same order, both within the grains and at the grain boundaries. These conditions are stringent and are obtained by the process of *mechanical alloying* (e.g. Gilman & Benjamin 1983), which I regard as using a composite principle to make the desired microstructure. Metal-alloy powder, ceramic powder and a processing control agent (PCA), often a wax or a soap, often based on stearic acid, are ground together in a ball mill. The PCA is chosen to lubricate, to prevent welding of the metal particles to assist fracture of the ceramic and finally, by combining with the metals present to form a carbide or oxide dispersed strengthener. The powders so produced are compacted by conventional means of handling powders.

The production of macrodefect free cement, MDF, is a more striking example of composite processing; here there is no compaction stage. The ideal microstructure of a cement is the same as that required of a ceramic: maximum particle packing, minimum volume of porosity and no large voids. This is achieved (see, for example, Birchall 1983) by use of a water-soluble polymer that has the function both to attach itself to the cement particles and to act as a lubricant under pressure. A readily deformable dough is formed that must be sheared so as to separate the cement particles. The dough can be processed by moulding extrusion or calendering (conventional polymer technology). Once the cement is formed to shape and hardened by the conventional water–cement reaction, the polymer present to the extent of some 7%, may be left in or burnt out.

Naturally, the use of plasticizers in polymer processing is well known where an oil or other additive is used to assist the manipulation of the molecular chains. I am calling composite processing the use of a fluid or readily deformable solid to disperse and arrange particles of much larger dimension.

Adequate substitutes for sanitary-ware ceramics can be made by producing very highly filled polymers containing 72% by mass or 55 vol. % of silica sand in methylmethacrylate fluid. The mixture is very easily cast if attention is paid to the range of particle sizes of the sand and the rheology of the polymer coupling agent; the commercial material is known as Asterite. Similarly a material called synthetic granite, which consists of 80–90 vol. % of granite in epoxy resin, forms a castable composite that may be used for machine tool beds.

A good example of composite processing is provided by what Ray (1978) calls *reconstructive processing* in which a naturally occurring mineral is dissected by chemical methods (it is probably essential to use chemical methods because there is apparently a lower limit to the size of particle that can be produced by comminution or crushing (see, for example, Kendall 1978; Hagan 1981) and then reassembled to the required shape. Air or voids can be introduced in the final stages to make a foam (Ballard & Rideal 1983). Other methods similar to these were developed in the 1960s, when it was thought that whisker crystals would provide a new class of composite material, and both asbestos and paper are made in this way.

Because of the increasing interest in the use of ceramics where the high processing temperatures necessary are a disincentive, there is a good deal of interest in methods such as these in efforts to produce rapid, energy-lean methods of processing of high-melting-point materials. I expect the use of these to grow greatly in the 1990s. The various forms of phosphoric acid are ideal media for dispersing a ceramic and later reacting it to form a solid. In principle, a melt of a metal that melts at a relatively low temperature, like magnesium or aluminium, might be used to disperse a ceramic followed by oxidation of the metal to form a high-melting-point matrix containing the ceramic. The recently announced process of encouraging the oxidation of Al to form 'lanxide'-type composites of Al_2O_3 dispersed in aluminium (Aghajanian *et al.* 1987) is another good example.

8. THERMAL CONDUCTIVITY

Composites have a rather special part to play in providing materials both of exceptionally high thermal conductivity and of exceptionally low thermal conductivity, both important properties for an energy-lean future. The thermal conduction of all materials approaches zero at 0 K passes through a pronounced maximum at a temperature less than room temperature and then decreases again at higher temperature (see, for example, Berman 1976).

It is not often recognized that the strongly covalently bound solids with light atoms possess higher thermal conductivities than do metals, for example that of sapphire exceeds that of Cu, and hence on a specific mass basis has a much larger specific conductivity. Values for a number of materials as a function of temperature are shown (figure 6). For metals the thermal conductivity in practical situations is often lowered by surface oxide films. Diamond is the best conductor but a much cheaper form of hyperconductor is graphite fibre that possesses a thermal conductivity parallel to its axis of 1380 $W\,m^{-1}\,K^{-1}$ (cf. copper 550 $W\,m^{-1}\,K^{-1}$ at the same room temperature) (Piraux *et al.* 1984). Such fibres can be doped to either enhance or decrease the electrical conductivity. According to Allen & Issi (1985) composites can be prepared with thermal conductivities of 750 $W\,m^{-1}\,K^{-1}$ and electrical conductivity of up to $5 \times 10^3\ (\Omega\,m)^{-1}$; this electrical conductivity is about the same as that of copper.

The very high thermal conductivity of the high-melting-point inorganic solids only occurs if they consist of perfect crystals. Heat transport through a solid occurs primarily by photon or electron transport. The heat flux depends strongly on the existence of chemical and structural imperfections and particularly on the presence of pores and of cracks. The same materials therefore, because they can exist stably even at elevated temperatures in a highly imperfect crystalline form (sometimes amorphous), can also, with proper attention to the microstructure, provide the lowest thermal conductors.

To provide the lowest possible thermal conductivity in a solid, one must minimize (*a*) solid conduction, (*b*) gaseous convection, (*c*) transmission of infrared radiation and (*d*) *gaseous* molecular conduction. The condition (*a*) is attained by using highly imperfect inorganic dielectrics; (*b*) by ensuring the presence of small voids so that convection is eliminated. Process (*c*) is the dominant conduction process at temperatures above 100 °C because of Stefan's law. It must be reduced by incorporating opacifiers: semiconductors of the correct band-gap (for

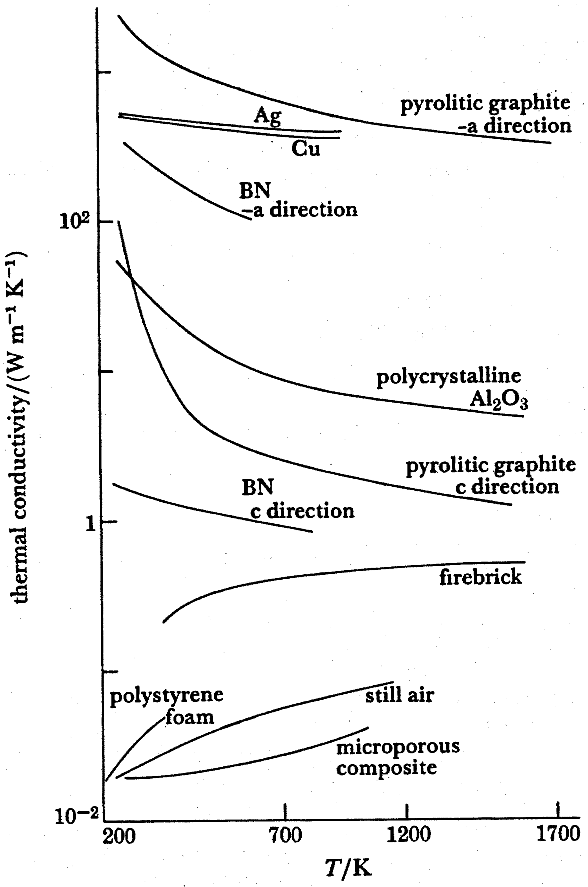

FIGURE 6 Thermal conductivity of various materials as a function of temperature; data from Parrott & Stuckes (1975).

example carbon black) or scatterers with high refractive index (metallic oxides). The result is a solid (foam) containing 90% voids. One can reduce the conductivity further to less than that of still air by ensuring that the distance between walls of the foam is less than the mean free path of still air, 100 nm at STP. The resulting inorganic foam is of course very weak and fibres are added to give it sufficient strength. It is an archetype of inorganic foam usually made from a microporous silica; some of the principles involved in making such a material are discussed by Dickson (1975). Composite principles have been used to hold air of sufficiently small particle size in place as an engineering material.

I am very grateful to J. Aveston, J. Lockett, L. N. McCartney and S. L. Ogin for comments on the manuscript, and to G. Ratcliff and P. Dickson for permission to use unpublished results.

REFERENCES

Aghajanian, M. K., Macmillan, N. H., Kennedy, C. R., Luczsz, S. J. & Roy, R. 1987 Properties and microstructure of selected lanxide composite materials *J. mater Res.* (In the press.)

Almond, E. A. 1983 Deformation characteristics and mechanical properties of hardmetals. *In Science of hard materials* (ed. R. K. Viswanadhan, D. J. Rowcliffe & J. Gurland), p. 517. New York: Plenum Publishing Corporation.

Aveston, J., Cooper, G. A. & Kelly, A. 1971 in *Conference Proceedings, National Physical Laboratory: The Properties of Fibre Composites*, pp. 15–26. Guildford IPC Science and Technology Press Ltd.

Ballard, D. G. H. & Rideal, G. R. 1983 *J. mater Sci.* **18**, 545.

Baral, D., Ketterson, J. B. & Hilliard, J. E. 1985 *J. Appl. Phys.* **57**, 1076.

Berman, R. 1976 *Thermal conduction in solids.* Oxford University Press.

Bickerdike, R. L., Clark, D., Easterbrook, J. N., Hughes, G., Mair, W. N., Partridge, P. G. & Ranson, H. C. 1985 *Int. J. rapid Solidification* **1**, 305.

Birchall, J. D. 1983 *Phil. Trans. R. Soc. Lond.* A**310**, 31.

Bonfield, W., Behiri, J. C., Doyle, C., Bowman, J. & Abram, J. 1984 *Hydroxyapatite reinforced polyethylene for bone replacement in biomaterials and biomechanics* (ed. P. Ducheyne, G. van der Perre & A. E. Aubert). Amsterdam: Elsevier.

Brown, L. M. 1979 *In Proc 5th International Conference on Metals and Alloys* (ed. P. Haasen, V. Gerold & G. Kosterz), vol. 3, p. 1551. Oxford: Pergamon Press.

Chou, T. W., Kelly, A. & Okura, A. 1985 *Composites* **16**, 187.

Dickson, D. J. 1975 Microporous thermal insulation. Report no. ECRC/M859, Electricity Council Research Centre.

Gilman, P. S. & Benjamin, J. S. 1983 *Rev. mater. Sci.* **13**, 279.

Hagan, J. T. 1981 *J. mater. Sci.* **16**, 2909.

Hannant, D. J. 1978 *Fibre cements and fibre concretes.* Chichester: J. Wiley and Sons Inc.

Henein, G. E. & Hilliard, J. E. 1983 *J. appl. Phys.* **54**, 728.

Kendall, K. 1978 *Nature, Lond.* **272**, 710.

Kelly, A. 1985 *Composites Sci. Technol.* **23**, 171.

Koehler, J. S. 1970 *Phys Rev* B**2**, 547.

Lehoczky, S. L. 1978 *J. Appl. Phys.* **49**, 5479. (see also *Phys. Rev. Lett.* **41**, 1814 (1978)).

Majumdar, A. J. 1970 *Proc R. Soc. Lond.* A**319**, 69.

Marshall, D. B., Cox, B. N. & Evans, A. G. 1985 *Acta metall.* **33**, 2013.

Meetham, G. W. 1982 *Metall. Mater. Technologist* **14**, 387.

McCartney, L. N. 1986 *Proc. R. Soc. Lond.* A **409**, 329–350.

McLean, M., Quested, P. N., Henderson, P. J. & Menzies, K. 1982 Development of the $\gamma = \gamma' Cr_3C_2$ in situ composites. In *In situ composites IV* (ed. F. D. Lemkey, H. E. Cline & M. McLean). New York: North Holland.

Parrott, J. E. & Stuckes, A. D. 1975 *Thermal conductivity of solids.* New York: Pion Ltd. (See also references therein).

Piraux, L., Nysten, B., Haqueune, A., Issi, J.-P., Dresselhaus, M. S. & Endo, M. 1984 *Solid St. Commun.* **50**, 697.

Pope, G. G. 1985 Structural materials in aeronautics: prospects and perspectives. RAE technical report no. 85077.

Prevorsek, D. C. 1982 Recent advances in high strength fibres and molecular composites in polymer liquid crystals (ed. A. Ciferri, W. R. Kingbaum & R. B. Meyer), pp. 329–376. New York: Academic Press.

Rabinovitch, M., Stohr, J. F., Khan, T. & Bibring, H. 1983 Directionally solidified composites for application at high temperature. In *Fabrication of composites* (ed. A. Kelly & S. T. Mileiko) Amsterdam: North Holland.

Ray, N. H. 1978 *Inorganic polymers.* London: Academic Press.

Takanyagi, M., Takayuki, O., Masonori, M. & Takashi, K. 1980 *J. Macromolec. Sci. Phys.* B **17** (4), 591.

Wiederhorn, S. & Tighe, N. 1984 NBS Technical report no. AFOSR 84–00013.

Discussion

F. E. Buresch (*University of Stuttgart, F.R.G.*). During his excellent and comprehensive review about composites for the 1990s Dr Kelly shows a figure concerning damage in a bend specimen of a laminated composite. My question concerns relations between damage and stochastic distribution of critical flaws and their influence on the strength of laminated structures.

With respect to one or multiphase ceramics it is well known that the strength decreases with the $1/m$-power of the volume of an unnotched component. This is due to the stochastic distribution of critical flaws. On the other hand, because of the damage zone in front of a critical crack the strength of a component or specimen decreases to zero with the $\frac{1}{4}$-power with decreasing specimen volume if this volume is smaller than the volume of the damage zone V_m. This follows from the path-dependent J-integral.

Thus theoretically in a diagram which shows the related strength S_c/S_m as a function of the related volume V/V_m, S_c/S_m equals one if V/V_m is one and decreases for lower and higher values of V/V_m as mentioned above. Here V_m and S_m are the volume of the damage zone and the cohesive strength of the material respectively. This behaviour was also observed experimentally.

Are these dependencies between strength and volume that were known from ceramics also observed for fibre-infiltrated composites?

A. Kelly. The size of the damage zone to be found at the end of a notch or crack in a composite and its dependence on microstructural parameters are discussed clearly by Potter (1978). For specimens larger than the size of the damaged zone but not very much larger, failure is controlled by the damaged zone and the gross tensile stress at failure falls with increasing notch size (or would increase with decreasing specimen size for a given notch length) until, for very large notches, the strength is determined by the elastic stress concentration factors of the notch.

So far as the strength of an *unnotched* composite is understood, if m is the value of the Weibull modulus of the fibres, then when these are introduced in to a composite, the value m is replaced (roughly) by km, where k is the critical number of breaks that must occur in adjoining fibres (nearest neighbours roughly) before total failure of the composite occurs. The value of k is usually three to four in practical cases.

Additional reference

Potter, R. T. 1978 *Proc. R. Soc. Lond.* A **361**, 325.

R. H. Biddulph (*Borax Research Ltd*, *Surrey*, *U.K.*). How are these microlayer materials joined?

A. Kelly. Microlayer materials can be joined in the same way as other composites. They can be welded, and the shape of specimen for efficient welding of joints is all important.

With respect to vapour-deposited aluminium alloys, in general, pretreatments are necessary for welding that will be different from those for conventional alloys because of, for instance, the large content of chromium and different oxidations propensities of the components. If interested, follow the matter up with Mr R. W. Gardener of the Procurement Executive of the Ministry of Defence at Farnborough.