



National Physical Laboratory

**THERMAL PROPERTIES OF COMPOSITE MATERIALS -
MEASUREMENTS, MODELS AND THERMAL EXPOSURE
DERIVED CHANGES IN MMCs AND CMCs**

by

R Morrell

Centre for Materials Measurement and Technology

October 1995

**THERMAL PROPERTIES OF COMPOSITE MATERIALS -
MEASUREMENTS, MODELS AND THERMAL EXPOSURE
INDUCED CHANGES IN MMCs AND CMCs**

by

R Morrell

Summary

A review of thermal property models for composite materials is given, together with examples from the literature of their applicability. Particular attention is paid to the ability of models to predict changes in behaviour with changes in microstructural detail that might come about as a consequence of thermal, mechanical or thermomechanical service.

It is concluded that at the present state of knowledge, modelling the complexity of composites has associated uncertainties to allow prediction of changes in properties of metal matrix and ceramic matrix composites resulting from thermal or thermomechanical exposure. Measurement of property changes remains crucial for the design and lifeing of these materials.

Examination of the extant models suggests that thermal conductivity/thermal diffusivity measurements, particularly the latter, offer the best potentially non-destructive method of identifying significant changes in composite interface properties in all cases except where the reinforcement has a very low thermal conductivity compared with the matrix, in which case changes to the interface have little overall effect.

Thermal expansion measurement, while important for determining hysteresis effects in thermal cycling and has some sensitivity to changes in interfacial conditions, is normally a destructive test and is a more complex property controlled by thermoelastic effects. These make interpretation of changes more difficult, especially for the case of mechanically relaxing matrices.

© Crown Copyright, 1995

(With the exception of Figure 1 to 3, published by permission of the original publishers)

Reproduced by permission of the Controller of HMSO

National Physical Laboratory Management Ltd
Teddington, Middlesex, UK, TW11 0LW

ISSN 1361-4061

No extracts from this report may be published without the prior written permission of Managing Director, National Physical Laboratory. The source must be acknowledged.

Approved on behalf of Managing Director, NPL, by Dr M K Hossain, Director, Centre for Materials Measurement and Technology

Signature of (principal) author

.....*R. Russell*.....

Date.....*21/2/96*.....

Signature of Head of Division

.....*M. K. Hossain*.....

Date.....*20/2/96*.....

CONTENTS

	INTRODUCTION	Page . 5
2	THERMAL EXPANSION	
2.1	Test method summary	
2.1.1	Mechanical dilatometry	
2.1.2	Strain gauge techniques	
2.1.3	Interferometry	
2.1.4	Thermal expansion during thermal cycling	
2.2	Thermal expansion measurement of composites	
2.3	Problem areas	
2.4	Modelling of composites	
2.4.1	Definitions	
2.4.2	Models for particle dispersions	
2.4.3	Models for fibre reinforcement	
2.4.4	Evaluation of models with regard to microstructural damage	
2.5	Comparison of models with experiment	
2.5.1	Particulate composites	
2.5.2	Continuous fibre composites	
2.6	Conclusions	
3	THERMAL CONDUCTIVITY/THERMAL DIFFUSIVITY	18
3.1	Thermal conductivity measurement - general	18
3.2	Thermal conductivity measurement of composites	18
3.3	Thermal diffusivity measurement - general	19
3.4	Thermal diffusivity measurement on composites	19
3.5	Thermal conductivity modelling	20
3.5.1	Definitions	20
3.5.2	Models for spherical particle reinforcement	21
3.5.3	Models for platelet reinforcement	22
3.5.4	Models for fibre reinforcement	22
3.6	Experimental results	24
3.6.1	As-produced materials	24
3.6.2	Materials suffering thermal degradation	25
3.7	Conclusions	26
4	SPECIFIC HEAT	27
4.1	Specific heat measurement	27
4.2	Specific heat measurement on composites	27
4.3	Modelling of specific heat	27
4.4	Measurements of specific heat	28
5	SUMMARY OF DISCUSSION OF THEORETICAL MODELS AND SENSITIVITY TO CHANGES IN MICROSTRUCTURE WITH THERMAL EXPOSURE	28
	Acknowledgement	30
	References	35
	Figures	38

1. INTRODUCTION

This review forms part of the Workplan of the project Design of Composite Components 2 - Thermal Properties, sponsored by EE Division of the Department of Trade and Industry. It concentrates on metal-matrix (MMCs) and ceramic-matrix composites (CMCs), although reference is made in places to polymer matrix composites (PMCs).

The long-term behaviour of metal-matrix and ceramic-matrix composites under mechanical and/or thermal loading is a key issue in their usability as engineering materials. These materials may not illustrate stable behaviour, and thus from a design point of view it is essential to understand these changes. The purpose of this review is to assess:

the effect on the thermal properties of changes that might take place in the microstructure, particularly at matrix/reinforcement interfaces, which might influence performance;

the uncertainties of measurement of thermal properties using typical methods

the ability of models to predict changes in thermal properties

The principal thermal properties of interest are thermal expansion (α), and thermal conductivity (λ) or thermal diffusivity (a). The last two are linked through the density (ρ) and specific heat (C_p):

$$\lambda = a \rho C_p \quad (1)$$

These properties are sensitive not only to the matrix and reinforcement types in composites, but also to their spatial arrangement and to the interface between matrix and reinforcement. Thus the properties of a composite are complex functions of their make-up, and are likely to be highly dependent on their manufacturing conditions and on any changes that take place in subsequent service. Table 1 lists service conditions of interest to industry for various types of MMCs and CMCs.

The test methods available to determine thermal properties are well-established, although there may be some limitations when dealing with anisotropic materials, or with materials available only in thin sections. In each case, the methods have experimental limits on the accuracy of determinations of properties. These limits will determine whether structural changes in composites are likely to be detectable by measuring changes in thermal properties. This report reviews the typical accuracy levels, and compares them with changes that are expected from theoretical models and with a selection of results published in the literature.

2. THERMAL EXPANSION

2.1 Test method summary

Thermal expansion can be defined as the fractional change in length of a body as it is heated and cooled. It can be expressed as the tangent slope of a plot of fractional length changes against temperature (usually known as the *expansivity*), but from an engineering point of view it is usually more convenient to use the change in length from a given temperature, e.g. 20 °C or 25 °C, to an upper temperature. The *mean expansion coefficient* is then the fractional change in length per unit temperature interval, which is usually numerically different from

the expansivity at the upper temperature.

Normally, expansion coefficients are quoted on the assumption that the material behaves reproducibly over the temperature range of measurement, but clearly the result of a measurement can be affected by irreproducible changes, such as annealing, creep, phase transformations, etc. In such cases considerable caution needs to be exercised in the recording and use of thermal expansion data. From the design point of view, a clear distinction needs to be made between true reversible thermal expansion effects, and any irreversible dimensional changes occurring as a result of thermal exposure.

There is in principle a variety of methods of determining thermal expansion characteristics, such as mechanical dilatometry, interferometry, telemicroscopy and strain gauges. Of these, mechanical dilatometry is the most commonly available, and the most widely used in materials science. Interferometry can give a greater degree of accuracy than dilatometry. Telemicroscopy is uncommon, and suitable for large dimensional changes only, and the use of strain gauges is rarely reported.

Mechanical dilatometry

In this technique, the change in length of a test-piece as it is heated and cooled is followed by a mechanical probe connected to a displacement measuring device. By correcting for the expansion characteristics of the system in which the test-piece is held, the behaviour of the test-piece can be deduced. The accuracy of the method is dependent on the mechanical repeatability of determining the expansion of the test-piece, and hence on the stability of the system and thus on its design. The temperature homogeneity and the accuracy of temperature measurement are also important. Heating rates should be low (or a series of temperature steps can be used) to minimise thermal lag effects which can lead to errors unless corrected for. There is a variety of standards in place for this technique, but of varying degrees of accuracy in the method depending on purpose. That developed for advanced technical ceramics, recently published as EN 821-1, is the most comprehensive and pays attention to appropriate calibration routines for accurate determinations.

Estimation of errors in mechanical dilatometry is not straightforward, since they derive from many sources, a major one being the mechanical stability of the test-piece in the apparatus. Practical experience has shown that when measuring a completely thermally stable material the accuracy of the fractional length change is limited to typically $\pm 10 \times 10^{-6}$ (10 ppm) or $\pm 0.1 \times 10^{-6} \text{ K}^{-1}$ in mean coefficient when measured over a 100 K temperature interval, as a result of accumulated errors in calibration and the lack of perfect mechanical repeatability. Over a wider temperature range (e.g. 25-400 °C) the accuracy expressed in this way is improved, and typically $\pm 0.05 \times 10^{-6} \text{ K}^{-1}$ may be achieved. For typical MMCs and CMCs, quoted expansion coefficients determined by mechanical dilatometry are thus unlikely to be more accurate than of the order $\pm 1\%$. These errors may be greater for materials with high expansion coefficients (e.g. $> 20 \times 10^{-6} \text{ K}^{-1}$) since the measured displacements are much larger, and the accuracy of temperature measurements becomes more important. Similarly, for low expansion materials, percentage errors may be larger than the above estimates since the potential calibration and mechanical errors become a major part of the measurement.

Strain gauge techniques

Strain-gauges and fixing techniques suitable to the temperature range required may also be used to determine thermal expansion, although the sensitivity of such a method is likely to

be no better than conventional mechanical dilatometry due to questions of gauge stability and electrical noise. There are also questions of gauge calibration for anisotropic materials. In composites, the averaging effect over the scale of the reinforcement is important, and large gauges would be preferred. Strain gauging does offer the opportunity to measure several directions simultaneously, which dilatometry does not do.

Interferometry

Improving upon the accuracy and repeatability of dilatometric measurement to the level of, say, 0.1% in coefficient or ± 1 ppm in total expansion requires that the displacement measuring system has much greater stability and resolution. This can be achieved by use of direct interferometric methods (i.e. with the light beams reflecting directly on the test-piece or from mirrors fixed to the test-piece, not by recording the push-rod displacement interferometrically as in some commercial instruments), but at this level there are usually accompanying difficulties caused by the irreproducibility of thermal cycling stability of the test-piece and air convection effects if the apparatus is not held under vacuum. A large accurately shaped test-piece is needed in order to obtain positional stability of reflecting surfaces, and this is often not viable, e.g. for fibre-reinforced composite materials which tend to be in sheet form. Additionally, increasing the test-piece size leads to longer thermal equilibration periods, and overall to slower and more expensive testing.

An optical means of measuring strain in tensile creep test-pieces using a system which detects the change in separate of flags attached to the gage length (e.g. the Zygo interferometer) could in principle also be used for measuring thermal expansion. Resolution is claimed to be typically $\pm 1 \mu\text{m}$. Assuming a 20 mm gage length in a material of mean expansion coefficient $10 \times 10^{-6} \text{ K}^{-1}$, a 100 K temperature rise produces a fractional size increase of 10^{-3} compared with a resolution of 5×10^{-5} . The method is therefore unlikely to have an accuracy of determining expansion coefficient to better than $\pm 5\%$.

Thermal expansion during thermal cycling

None of these techniques are ideal for following progressive size changes consequent on thermal cycling. They all rely either on slow temperature ramping (e.g. 2 K/min) or a series of temperature steps with thermal equilibration holds. Inhomogeneous temperature leads to significant errors in dimensions at the nominal specimen temperature. Strain gauges offer a possible solution provided they themselves and their adhesive are sufficiently stable.

2.2 Thermal expansion measurement of composites

Thermal expansion can be somewhat anisotropic in fibre-reinforced composites, but generally this poses no problems in making measurements since test-pieces can generally be prepared for measurement in any relevant direction. In-house testing of a variety of materials has shown that representative test-pieces can be prepared quite readily. The main problem area is making through-thickness measurement of thin sheet. Ideally, mechanical dilatometry requires a certain length of specimen, typically 10-40 mm. The mechanical instability and calibration errors tend to be independent of the test-piece length, so that for very thin specimens they represent a large proportion of the total displacement recorded, leading to inaccurate results. One possible route is to make a test-piece from a number of sheet thicknesses by stacking and allowing the dilatometer pushrod to apply sufficient force to keep the stack in position. This has been found to work in principle, but the surfaces of the individual layers need to be flat to be mechanically stable. The plastic relaxation effects in

metal-matrix materials is likely to be exaggerated as contacts between the layers flatten at higher temperatures, and thus until good contact is achieved, the recorded behaviour may not be truly representative of that of the single sheet.

Problem areas

The key problem in defining reliable data is in materials which do not have stable expansion characteristics. Internal stresses between the matrix and the reinforcement develop on cooling from the nominally stress-free condition at the fabrication temperature. As a consequence of thermal expansion mismatch between matrix and reinforcement, the resulting thermal contraction behaviour depends on the maintenance of continuity of interfaces between matrix and reinforcement, and on any plastic flow occurring in either. In the absence of plastic flow or relaxation, the internal stresses are partitioned between reinforcement and matrix, and are a function of temperature only. The dimensional changes on subsequent heating and cooling are consistent and repeatable. On the other hand if, for example, the matrix yields under the influence of the internal stresses the thermal expansion behaviour may reflect elastic relaxations, work hardening effects, etc, depending on the temperature ranges over which tests are performed. Hysteresis may be seen between heating and cooling. Effects may be most marked with polymer composites due to glass-transition and viscoelastic phenomena. If interface debonding in UD materials or inter-ply delamination in laminates occurs, this may also lead to non-uniform behaviour with hysteresis on thermal cycling.

In addition, the thermal expansion behaviour of some types of polymer matrix composite is sensitive to moisture content and to any changes that take place during thermal cycling in the apparatus. Control of humidity around the test-piece may be critical.

2.4 Modelling of composites

Definitions

The following symbols are used in the text:

$\alpha_{eff,l,t}$	=	effective linear thermal expansion coefficient of composite, subscripted for longitudinal or transverse directions
α_m	=	linear thermal expansion coefficient of matrix material
α_r	=	linear thermal expansion coefficient of reinforcing material
β_{eff}	=	effective volume thermal expansion coefficient of composite
β_m	=	volume thermal expansion coefficient of matrix material
β_r	=	volume thermal expansion coefficient of reinforcing material
E_m	=	Young's modulus of matrix material
E_r	=	Young's modulus of reinforcing material
G_m	=	shear modulus of matrix material
G_r	=	shear modulus of reinforcing material
K_{eff}	=	effective bulk modulus of composite (ignoring anisotropy)
K_m	=	bulk modulus of matrix material
K_r	=	bulk modulus of reinforcing material
V_m	=	volume fraction of matrix
V_r	=	volume fraction of reinforcing material ($V_m + V_r = 1$)

The above symbols assume elastic and thermal expansion isotropy in both matrix and reinforcement. This will not always be the case, especially in some fibres, such as carbon fibres.

2.4.2 Models for particle dispersions

The simple rule of mixtures for instantaneous thermal expansion of an isotropic composite comprising a dispersion of reinforcement in a matrix is:

$$\alpha_{eff} = \alpha_m V_m + \alpha_r V_r$$

based on several simplifying assumptions, but a key one as far as MMCs and CMCs are concerned is that there is no non-elastic relaxation, such as plastic flow or internal microcracking. Similar terms can be added for other phases, such as interlayers. Dispersed porosity has little or no influence. However, this analysis does not take into account the potentially different elastic properties of matrix and reinforcement, which has the effect of modifying the partition of the thermal strains between matrix and reinforcement. The model of Turner (1946) incorporates bulk modulus K :

$$\alpha_{eff} = \frac{1}{3} \frac{\beta_m K_m V_m + \beta_r K_r V_r}{K_m V_m + K_r V_r}$$

There is a variety of other models incorporating either Young's, shear or bulk moduli of the individual components, and/or the effective values of the composite (see Taylor (1991)), which are valid for any reinforcement shape. Eshelby (1957, 1959) employed a mechanical model in which the thermal expansion behaviour was derived from the behaviour of the matrix when inclusions were subjected to size changes. Schapery (1968) has developed:

$$\frac{\beta_{eff} - 3\alpha_r}{3(\alpha_m - \alpha_r)} = \frac{K_m(K_r - K_{eff})}{K_{eff}(K_r - K_m)} \quad (4)$$

where K_{eff} is given by Hashin (1983) as:

$$K_{eff} = K_m + \frac{V_r}{1/(K_m - K_r) + 3V_m/(3K_m + 4G_m)} \quad (5)$$

Takahashi et al. (1985) have proposed the following for volume distributed spherical particles:

$$\beta_{eff} = \beta_m + \frac{K_r(3K_m + 4G_m)(\beta_r - \beta_m)V_r}{K_r(3K_m + 4V_r G_m) + 4G_m K_m V_m} \quad (6)$$

and for disc-shaped randomly orientated particles:

$$\beta_{eff} = \beta_m + \frac{K_r(4G_r + 4K_m)(\beta_r - \beta_m)V_r}{K_r(4V_r K_r + 3K_m) + 4V_m G_r K_m} \quad (7)$$

In a more general sense, for arbitrary arrangements of phase geometry, Hashin and

Shtrikman (1963) used a so-called variational approach to estimate the upper and lower bounds of any property subjected to uniform strains. Using the upper and lower bounds for bulk modulus for the composite bulk modulus K_{eff} , upper and lower bounds of the volumetric expansion coefficient:

$$\beta_{eff}^{(-)} < \beta_{eff} < \beta_{eff}^{(+)} \quad (8)$$

are obtained where the bounds are given by inserting into Equation 4 the following:

$$\text{Lowerbound: } K_{eff}^{-} = K_m + \frac{V_r}{1/(K_r - K_m) + 3V_m/(3K_m + 4G_m)} \quad (9)$$

$$\text{Upperbound: } K_{eff}^{+} = K_r + \frac{V_m}{1/(K_m - K_r) + 3V_r/(3K_r + 4G_r)} \quad (10)$$

Hashin (1983) has discussed further developments of this theory. The physical reality of these bounds is that they relate to the extremes of spatial arrangement of the reinforcement from being a continuous network to a series of isolated particles.

Note that all these models assume that reinforcement and matrix have isotropic elastic and thermal expansion properties, and that there is no effect of particle size.

Comments on modelling assumptions

There are in-built assumptions in these models:

- both matrix and reinforcement have isotropic elastic properties
- the reinforcement has a well-defined geometry such as a sphere or ellipsoid
- the interface between matrix and reinforcement is mechanically continuous, even when the interface is under tension
- the system is always purely elastic
- the distribution of reinforcement is spatially uniform

Generally, most or all of these assumptions are not borne out in practice. In this respect, such models can therefore only provide a guide to the expected value of α_{eff} . They cannot be used to make reliable, accurate predictions without some assurance that the fundamental assumptions are met. As an example of the problem, Ledbetter and Austin (1991) tested a hot-rolled Al 6061/30% SiC_p composite and found that it had anisotropic thermal expansion properties that were not accurately predictable, even from some of the complex bound equations. Further detail is given in 2.5.1.

2.4.3 Models for fibre reinforcement

As with the isotropic particulate reinforcement case, all models have some limitations in terms of the simplifying assumptions made, and the progressive refinements that have been developed are an indication of their unsatisfactory predictive capability.

A special case of Schapery's Equation 4 for unidirectional fibrous reinforcement is when the Poisson's ratio of fibre and matrix are assumed to be the same, giving for the longitudinal direction (subscript l):

$$\alpha_{eff,l} = \frac{E_m \alpha_m V_m + E_r \alpha_r V_r}{E_m V_m + E_r V_r} = \frac{\sum E \alpha V}{\sum E V}$$

For the transverse direction in a transversely isotropic composite (subscript t), Equation 4 reduces to:

$$\alpha_{eff,t} = (1 + \nu_m) \alpha_m V_m + (1 - \nu_r) \alpha_r V_r - \alpha_{eff,l} (\nu_r V_r + \nu_m V_m)$$

where the last term in brackets is the rule of mixtures Poisson's ratio of the composite. A further factor arises in that fibrous reinforcement cannot necessarily be considered to have isotropic thermal expansion or elastic characteristics as a result of the crystalline structure developed. Levin (1967) developed different explicit formulations for unidirectional fibrous composites:

$$\alpha_{eff,l} = (V_r \alpha_r + V_m \alpha_m) + \left(\frac{\alpha_r - \alpha_m}{\frac{1}{K_r} - \frac{1}{K_m}} \right) \left(\frac{3(1 - 2\nu_{12})}{E_{11}} \frac{V_r}{V_m} - \frac{V_m}{V_r} \right)$$

$$\alpha_{eff,t} = (V_r \alpha_r + V_m \alpha_m) + \left(\frac{\alpha_r - \alpha_m}{\frac{1}{K_r} - \frac{1}{K_m}} \right) \left(\frac{3}{E_{11}} \frac{3\nu_{12}(1 - 2\nu_{12})}{V_r} - \frac{V_r}{V_m} \right)$$
(14)

where E_{11} , K_{23} and ν_{12} are the effective composite uniaxial modulus, plain strain bulk modulus and axial Poisson's ratio respectively. These equations have been shown to be equivalent to those of Eshelby (1957, 1959) for short-fibre MMCs. Similar relationships have been developed by Rosen and Hashin (1970). For anisotropic fibres, Chamberlain, quoted by Rogers et al. (1977), has shown that the rule of mixtures equation can be used without modification for the longitudinal direction if the axial Young's modulus and expansion coefficient of the fibre are used. However, the transverse equation changes to:

$$\alpha_{eff,t} = \alpha_m + \frac{2(\alpha_r - \alpha_m)V_r}{\nu_m(F - 1 - V_m) + (F + V_r) + (E_m/E_{r,l})(1 - \nu_{r,1,2})(F - 1 - \nu_m)}$$
(15)

where F is a fibre packing factor = 0.9060 for a hexagonal array and 0.7854 for a square array.

Hsueh and Becher (1988) have examined a composite cylinder thermoelastic model combining thermal and mechanical strains resulting from mismatch in thermal expansion. Effective axial and transverse thermal expansions are calculated from the thermoelastic solution by dividing

the axial and transverse matrix strains by the temperature change ΔT . For the case of the matrix and fibre elastic moduli being the same, their equations reduce to those for the simplest rule of mixtures.

McCartney (1992a) has extended the above formula to the case of multiple systems of transversely isotropic concentric cylinders so that the effects of fibre architecture and coatings can be studied. Furthermore, in cross-ply laminates subject only to in-plane loading the resultant composite expansion coefficients can be predicted from the unidirectional case (McCartney 1992b). More recently, these formulations have been demonstrated for Ti/SiC_f composites (McCartney and Morrell (1995)).

A curiosity arises for uniaxial models when the elastic modulus of the fibre is much larger than that of the matrix (e.g. notably in fibre-reinforced polymers, e.g. CVD SiC fibres in epoxy resin (Tandon and Chatterjee (1991), but also measured experimentally in a BORSIC-Al unidirectional composite (Kreider and Patarini (1970)). For low volume fractions of fibre, typically up to 0.10-0.15, the effective transverse expansion coefficient of the composite is greater than that of the matrix or fibre itself, whereas the rule of mixtures would dictate that it should be intermediate between fibre and matrix. This has been explained (Hsueh and Becher (1988), Clyne and Withers (1993)) as being due to the fact that on increasing the temperature the effective thermal strain is a combination of unconstrained thermal expansion of the matrix and the elastic strain due to changes in internal thermal stress. In conditions where the elastic strain has the same sign as the unconstrained matrix thermal expansion, the strains add, and the net expansion coefficient is larger than that of the matrix. A high level of matrix axial stress induces a high level of transverse Poisson strain which more than compensates for the reduction in natural thermal expansion induced by low transverse expansion fibres.

It cannot always be assumed that the thermal expansion coefficient or the elastic properties of fibres themselves are isotropic. In particular, carbon fibres may be anisotropic in both properties. Equations such as those of Schapery, have to be modified to take account of this anisotropy (Hancox and McCartney (1990)), and experimental determinations have allowed the anisotropy to be determined.

A further special case is that of short-fibre composites in which there is a length of fibre which debonds as a result of a weak interface. This has been developed through the so-called "shear-lag" theory. An "efficiency factor" can be introduced to Equation 8 which is related to the ratio of the fibre length to the critical length defined by the fibre radius, its tensile strength and the fibre-matrix bond shear strength (Marom and Weinberg (1975), Marom and Gershon (1975), Morimoto et al. (1984), etc.).

Modelling of short-fibre aligned composites (Weissenbek and Rammerstorfer (1993)) has shown that axial and transverse expansion behaviour will depend on the geometry of the staggering of fibres. Evaluating this model using the properties for a aluminium alloy/glass fibre system has demonstrated thermal expansion hysteresis. The effect of aspect ratio distribution has been modeled by Takao and Taya (1987) for Al/SiC_w and epoxy/carbon fibre systems.

Comments on modelling assumptions

For uniaxial composites using round-section fibres, simple geometrical models have some realism. The progressive refinement of models to allow for different axial and transverse

properties, for yielding in the matrix, for matrix cracking, for non-elastic interface properties has meant that the prospects for prediction of performance are now quite good. However, to use such models requires data on fibre properties which are difficult to measure, for example, transverse elastic and thermal properties of fibres, and the yield characteristics of matrices that may have been affected by reaction with fibres or their coatings. Careful experimental modelling of composites may allow the transverse properties of fibres to be deduced indirectly from reliable models, rather than needing to measure them directly.

For crossply fibre materials models are inevitably more complex, especially if matrix cracking occurs. Finite element modelling of fibre/matrix systems offers an opportunity to check the results of mechanical models, and may be able to provide separate verification of the predictions. At present, measurement work on MMCs and CMCs to assess the validity of predictions is very limited indeed.

2.4.4 Evaluation of models with regard to microstructural damage

Particulate composites

With the exception of the short-fibre model, the models described above assume that the interface between the matrix and reinforcement remains continuous. If this is not the case, when the expansion coefficient of the reinforcement is greater than that of the matrix, e.g. in some CMCs, the reinforcement tries to shrink more on cooling from a stress-free condition at elevated temperature, and places the interface into radial tension. The degree to which the interface can survive this tensile stress determines the overall behaviour. If the interface debonds, the reinforcement no longer has an influence on the overall expansion characteristics at lower temperatures, which are then similar to those of the matrix alone. Conversely, if a weak debonded interface oxidises or otherwise changes such that a rigid bond is produced where formerly there was none, the expansion coefficient will increase because of a contribution from the reinforcement. The intermediate situation of partial delamination with rehealing on heating and re-cracking on cooling can lead to thermal expansion hysteresis and to thermal cycle ratchetting.

On the other hand, if the matrix expansion coefficient is higher than that of the reinforcement, such as in most hard-phase reinforced polymer composites and MMCs, and in some CMCs, the interface is placed into radial compression on cooling from a stress-free temperature. In this case, unless either the matrix or the reinforcement undergoes stress relaxation by deformation or the matrix microcracks, the interface cannot delaminate, and the thermal expansion characteristics remain essentially constant. However, often the matrix cracks radially about each fibre.

In the case of soft-matrix MMCs, the behaviour during thermal cycling is complicated by the rate at which internal thermal mismatch strains can be relaxed by plasticity or creep. At elevated temperatures where the rate of relaxation is fast compared with the timescale of observation, the net expansivity is essentially that of a simple volume fraction based rule of mixtures since no thermal mismatch remains involved. As the temperature is lowered, and internal strains begin to build up, the expansion coefficient begins to change towards that modelled by a non-ductile rule of mixtures taking thermal mismatch into account. Since the rate of relaxation is a function not only of temperature and stress level, but also the degree of work hardening that has accumulated, precise levels of expansivity cannot be readily determined, and may even depend on the length of time between heating and cooling cycles. Apparent expansivities may be lower in the first thermal cycle performed on previously

uncycled material, and increase thereafter, because of the relaxation that occurred before starting testing. Hysteresis and thermal ratchetting may also develop to a degree depending on the temperature cycling range because the matrix is in a work-hardened state on heating, but not on cooling, resulting in different internal stress states.

The use of the models for predicting numerically the extent of change in expansion coefficients with changes in the nature of interfaces or with transverse matrix cracking is thus complex. It requires knowledge of elastic and thermal expansion characteristics of all component phases, data which often do not exist with sufficient accuracy to obtain predictions which are better than rough estimates. The development of internal cracks or delaminations can lead to significant changes, and these are most likely to be detectable when matrix and reinforcement have a large thermal expansion differential, interface failure occurring especially with $\alpha_r > \alpha_m$ and radial matrix cracking especially with $\alpha_r < \alpha_m$. The development of interface phases during thermal treatment needs also to be taken into account.

In hard particulate MMCs, failure of the matrix is less likely than failure of the particles. It has, for example, been shown that tensile stressing of the material leads to plastic extension of the matrix and cracking of particles, the larger ones cracking transversely to the applied stress first and the smaller ones later as the plastic matrix strain is progressively increased. This reduces the consequent Young's modulus (e.g. Mochida et al. (1991), examining an 6061 Al/Al₂O_{3p} composite), and is likely to result in an increase in the expansion coefficient, especially in the direction of stressing, but no literature to prove this point has been identified.

Continuous fibre composites

Similar basic assumptions to the particulate model concepts apply also to those for fibre composites. In practice, with $\alpha_r < \alpha_m$, there is axial constraint on matrix shrinkage which produces large axial tensile forces leading to transverse matrix cracking in brittle matrices, such as CMCs. The crack spacing is related to the degree of mismatch, or indeed to the level of subsequently applied axial tensile stress. In unidirectional continuous fibre composites, the axial expansion coefficient should change from the rule of mixtures towards that for the fibres alone, since the matrix can no longer bear the internal stress. The radial expansion coefficient will also change also as a result of the loss of axial constraint on matrix blocks. At low volume fractions of fibres the implications of the phenomenon of unexpected increases in expansion coefficient for small fibre volume fractions explained above (Hsueh and Becher (1988), Clyne and Withers (1993)) can be extended to argue that the Poisson contraction effects of matrix onto fibre will be reduced, and thus at low volume fractions at least, the transverse expansion coefficient should reduce towards the rule of mixtures result, while at high volume fractions the effect may be negligible.

With $\alpha_r > \alpha_m$, the fibres tend to shrink away from the matrix placing the interface in tension and risking loss of continuity. However, if the fibre ends are not allowed to move relative to the matrix, the axial expansion coefficient will remain the same, as defined by the simple rule of mixtures (e.g. Eqn. 4 for $\nu_r = \nu_m$). However, in practice some relaxation or fibre breakage may occur, and this would tend to reduce the expansion coefficient towards that of the matrix. Similarly, the loss of interface continuity would mean that again the matrix would control behaviour, the fibres playing no role.

Thermal cycling effects

Normally, if the matrix and reinforcement remain elastic in behaviour, and no damage occurs, thermal expansion behaviour should be reversible and repeatable on thermal cycling. However, when the matrix is plastic or can microcrack, and can therefore relax some of the internal thermal stresses, or when permanent changes at interfaces occur, thermal expansion hysteresis can develop. An example of this behaviour is shown in Figure 1 for 30% Nicalon SiC fibres in an Al-3%Mg alloy (Masutti et al. (1990)). The composite is virtually stress free above about 800 K and, in the timescale of heating/cooling, measurement is approximately elastic below 450 K after the first cycle. The first cycle itself has a different shape on heating because of stress relaxation that has occurred during its previous excursion to liquid nitrogen temperature before testing.

In repeated cycling, behaviour depends on whether the matrix material retains consistent stress relaxation properties or workhardens. Progressive work hardening can lead to damage which is manifested as a progressive change in length with increasing number of cycles. This can be particularly marked in short-fibre composites, or where the composite is subjected to an applied stress during cycling. In the latter case, the applied stress adds to the thermal stresses and accelerates stress relaxation and creep.

2.5 Comparison of models with experiment

2.5.1 Particulate composites

Raghava (1988) has shown that for an epoxy resin filled with copper spheres, the composite expansion characteristics are most closely matched by equations like that of Schapery, Equation (4) for a wide volume fraction range of 10-40% by volume, while the simple Turner Equation (3) deviated considerably. However, Tummala and Friedberg (1970) used Sb-Pb composites to show that their own equation and the Turner equation were reasonable matches. Similar matching was later obtained for glass-TiO₂ composites (Tummala (1976)).

An interesting point has been raised by Scherer (1987) who suggests that the effective setting temperature, and hence the temperature range over which thermal stresses are built up, depend on the relative size of rigid reinforcement to that of the matrix. Thin layers of matrix material such as glasses or polymers are likely to suffer much higher stresses and therefore relax more during the viscoelastic stage of "setting" than thick layers. This might be expected to have some small effect on levels of internal stress, but to a first approximation are unlikely to affect composite thermal expansion behaviour.

In evaluating a hot-rolled Al/SiC_p material, Ledbetter and Austin (1991) tried to explain this in terms of equations for transversely isotropic media which showed a better prediction than simple rule of mixtures (20% inaccuracy) or isotropic elastic models (e.g. Eqn. 2 or 3, 10% inaccuracy). However, the problem remained that the microstructure was inhomogeneous. Most SiC particles tended to be aligned in groups in the plane of rolling, surrounding islands of matrix. Although a neutron scattering pole figure showed that there was no preferred *crystallographic* orientation of SiC grains, no attempt was made to verify whether there was an orientation dependence of the effective geometrical path length through SiC grains.

Taylor (1991), in reviewing other work, notes that there are numerous conflicting observations in the literature, and that reported results may well have to be treated with some circumspection since the material systems employed may not always behave in a

consistent manner. For example, fine particles may not completely disperse in a matrix, or may react with or dissolve into the matrix (e.g. in glasses) so that assumed volume fractions of reinforcement are larger than actual values.

An interesting factor considered by Sergo and Meriani (1991) is the so-called percolation threshold, when the reinforcing phase can no longer be considered to be individual particles, but a continuous path of reinforcement exists. They demonstrate this phenomenon using CeO_2 stabilised zirconia as a matrix and SiC particles and whiskers as the reinforcement. They note discontinuous departures from the rule of mixtures relationship for thermal expansion of the composite when the volume fraction is in the range 0.10-0.15. This result was correlated with a similar discontinuity in electrical conductivity/temperature behaviour, changing from being that typical of an insulator to that of a semiconductor. Their conclusion is that anomalous behaviour can occur in real systems which is outside the scope of simple models. This leads to uncertainties in the predictive power of modelling to identify correctly the likely changes in characteristics resulting from thermal exposure.

Reeves et al. (1991) examined the influence of reaction zones in Ti-10 vol% SiC_p composites producing microcracked layers of TiC and Ti_5Si_3 up to 1 μm thick. Small changes of the order of a percent or so in expansion characteristics were noted after thermal treatment at 950 $^\circ\text{C}$ for various periods, together with the development of slight hysteresis. It was estimated from modelling equations that the expansivity of the interface phase must be about $15 \times 10^{-6} \text{ K}^{-1}$ compared with $8 \times 10^{-6} \text{ K}^{-1}$ for the composite.

Xu et al. (1994) employed the simple rule of mixtures (Equation 2) to predict the expansion characteristics of the interface developed on the surface of 0.7 to 4 μm TiC particles in an aluminium matrix, and concluded that the particle size effect seen was due to different volume fractions of interface region involved. Although no third phase was found, lattice distortions had been noted, and the results are attributed to this phenomenon. By ascribing a volume fraction to the interlayer, a prediction of expansion characteristics was made, which was found experimentally to be close to that of TiC.

In cases where an all-brittle composite has been designed for specific thermal expansion behaviour, e.g. for zero thermal expansion using mixtures of positive and negative thermal expansion phases, or a single phase with positive and negative crystallographically anisotropic thermal expansion behaviour, it is often found that expansion coefficient and hysteresis are strong functions of grain size. Examples include magnesium dititanate (Kuszyk and Bradt (1973)), aluminium titanate (Ohya et al. (1987)), niobia and β -spodumene (Hawkins and Wolff (1983)), graphite/Pyrex (Douglas and Prewo (1983)).

2.5.2 Continuous fibre composites

While there are demonstrations that various models can represent the nominal behaviour of long-fibre composites, there has been little if any reported work so far on the effects of thermomechanically induced microstructural changes on thermal expansion behaviour.

For example, Rojstaczer et al. (1985) have demonstrated that for both longitudinal and transverse thermal expansion behaviour, Schapery's equations work well for unidirectional Kevlar/epoxy composites of various volume fractions. Eckel and Bradt (1990) report that an 4HS woven FP alumina fibre laminated CVI SiC matrix composite shows variable hysteresis in thermal expansion behaviour, which is matched by the Schapery rule of mixtures model

at 600-1000 °C, but departs from this model at lower temperatures. However, the data for individual components given in the paper suggest that no temperature variation of thermal expansion was taken into account. Lower thermal expansion Nextel 312 (mullite glass) and Nicalon SiC fibres did not show hysteresis, presumably due to a closer match with the CVI matrix. In contrast, Elkind et al. (1992) made detailed measurements of thermal expansion behaviour of SiC monofilaments and a borosilicate glass and found that the Schapery equation was indeed a good match up to a fibre volume fraction of 0.45.

Using extant data for the matrix and reinforcement, McCartney and Morrell (1995) have very recently verified experimentally models of thermal expansion of unidirectional and cross-ply laminates of Ti-SiC_f and obtained an excellent match.

2.5.3 Thermal cycling behaviour

Simple models ignore plasticity, microcracking or interface degradation under thermal cycling conditions. The added complexity that these factors introduce is difficult to deal with analytically. Daehn and Gonzalez-Doncel (1989) conducted a range of isothermal and thermal cycle stress/strain and creep determinations, and found that the apparent creep rate under thermal cycling was influenced by the applied stress in the range 5-20 MPa, and by the range of temperature. The net change per thermal cycle was insignificant under zero stress and low temperature ranges, but was much larger under applied stress, giving a net thermal expansion. The experimental results were compared with a shear deformation and thermal mismatch model, with reasonable matching. Zhang et al. (1990) undertook FEA modelling of repeated thermal cycling of Al/SiC_p MMC, and established that the progressive length change with thermal cycling through a temperature interval of 350 K modelled for a perfectly plastic Al matrix with 11 vol.% spherical SiC particles depended on the applied tensile stress in the range 4-30 MPa, and had a magnitude of between +30 and +5000 ppm. In comparing these figures with those determined experimentally on an Al/20 vol.% aligned SiC_w material by Daehn and Gonzalez-Doncel (1989), reasonable agreement was found.

Behaviour under zero stress may be different. For example, Kehoe and Chadwick (1991) found that for a squeeze-cast high-purity Al-Saffil fibre composite net length changes per thermal cycle ranged between near zero and -700 ppm, i.e. a shrinkage, depending on fibre volume fraction (Figure 2). Similar behaviour has been noted in NPL tests on Al 6061/SiC_p composites.

2.6 Conclusions

Thermal expansion modelling is thus complex and, in a practical sense, highly reliant on detailed mechanical properties of the individual phases and their crystallographic and spatial anisotropy. The accuracy of modelling can be quite effective in all-elastic cases with isotropic properties and spatial distribution, but becomes increasingly complex with:

- elastically anisotropic phases
- inhomogeneity and overall anisotropy
- phase changes
- mechanical relaxation of internal stress (ductile matrix, matrix cracking)
- changes in interface properties debonding, reactions, etc.).

Loss of interface continuity or matrix cracking can lead to hysteresis on heating and cooling, to permanent or even progressive changes. It thus seems difficult to predict trends with

potential thermally-originated degradation in detail. Nevertheless, thermal expansion measurements are sensitive to changes in the internal stress pattern in a composite. They can be used to determine matrix relaxation temperatures and progressive increases or decreases in length with thermal cycling and interface opening/closing behaviour. However, reliable distinction between mechanisms cannot be obtained using models because of the unknown parameters. Thus although in principle thermal expansion measurement could detect potentially serious damage in material microstructures, separating such effects from other influences might be practically difficult.

3. THERMAL CONDUCTIVITY/THERMAL DIFFUSIVITY

3.1 Thermal conductivity measurement - general

Normally this property is determined under steady state heat flow conditions such that the heat flow rate and temperature gradient through a defined thickness can be determined. For thermal conductivities greater than about $20 \text{ W m}^{-1}\text{K}^{-1}$ a bar method is suitable for materials available in bar form. The heat flow along the bar and the temperatures at several points are determined.

For materials with thermal conductivities in the range 5 to $50 \text{ W m}^{-1}\text{K}^{-1}$, especially for those available only in sheet form, a comparator method can be employed in which the test-piece is sandwiched between reference samples to form a composite bar. Assuming small or known thermal resistances at the interfaces, the thermal conductivity of the unknown is determined from the temperature of its faces and the calculated heat flow through it based on the temperature gradients in the reference samples. If the thermal conductivity is high, however, potential errors are also large since the layer interface properties have high significance.

For materials of low thermal conductivity, and those available only as thin sheet, some form of plate method is needed. In all methods, the principal sources of error are the thermal resistance at the surfaces, the non-uniformity of heat flow (lateral flow must be restricted if not eliminated), and temperature measurement. Overall accuracies depend on care and attention to the above points, but are seldom better than $\pm 5\%$ in the mean conductivity over the measurement temperature interval.

3.2 Thermal conductivity measurement of composites

Thermal conductivity of composites, especially fibre composites, can be highly anisotropic, perhaps by a factor of up to 100, e.g. in situations with highly conducting fibres and poorly conducting matrices. This creates problems of ensuring heat flow is restricted to the required direction, and may result in larger experimental errors than for isotropic materials.

Provided that the composite structure of the required test-piece is representative of the bulk material, there are no practical problems in principle with acquiring test-pieces from materials available as bars or thick-section sheet. However, as mentioned in 3.1, through-thickness measurement of thin but high thermal conductivity materials is prone to error because temperature differentials across the test-piece are small and difficult to measure. It is risky to bond several sheets together to form a thicker test-piece because the bond line may not be completely representative of normal material. Such geometries may be more appropriate for thermal diffusivity measurement.

Measurement of thermal conductivity of thin sheet in the plane of the sheet can be made directly by radial or linear heat flow methods, or indirectly using, e.g., a hot probe method. Indirect methods may yield results which are relatively inaccurate (possibly of the order $\pm 20\%$). Another possibility for materials of high thermal conductivity is to bond several sheets together to form a rod, and then to use the long-bar technique to obtain greater accuracy. In this case the interfaces between sheets play no role in the measurement.

3.3 Thermal diffusivity measurement - general

Nowadays, thermal diffusivity is more often measured on structural materials than thermal conductivity because it is quicker, cheaper, and capable of being used to very high temperatures. The most common method relies on a high-intensity heat pulse being applied to one face of a thin test-piece, usually using a single pulse laser. The temperature of the other face is monitored, either by thermocouple or preferably by a solid state IR detector, and the temperature transient curve is monitored. By analysis of this curve with appropriate corrections for finite pulse time and radiation loss effects, the thermal diffusivity can be derived. Usually, the analysis is based on the time to half of the maximum temperature rise ($t_{1/2}$), which is related simply to the thermal diffusivity (a) by:

$$a = \frac{1.38 L^2}{\pi^2 t_{1/2}} \quad (2)$$

where L is the thickness of the test-piece. The advantages of the method are its speed and the fact that the overall temperature rise can be small, and thus the thermal diffusivity relates to a narrow temperature range rather than to a mean result over a wider temperature range as determined by thermal conductivity methods. The principal factors affecting accuracy are the parallelism of the test-piece (ΔL), the homogeneity of the heat pulse over the test-piece area, and the appropriateness of corrections for finite pulse times and radiation losses. Figures of about $\pm 4\%$ are typically quoted. Reference materials are generally not needed, although checking the correct functioning of the system using a material with well-characterised thermal conductivity and specific heat is desirable.

The principal practical problem area is for measurement of thin-layer composites parallel to the fibre plane. It is normally necessary to construct a test-piece from a number of strips of material clamped together to form an area appropriate to the equipment such that the heat flow direction is along the desired direction in the composite. Any gaps in the test-piece can be filled with carbon black to prevent incoming laser energy directly affecting the transient detector. The representative nature of such built-up test-pieces may not be adequate with coarse-textured materials, such as woven fibre composites. Large potential errors of measurement could arise.

An advantage of the flash method is the need for moderately small test-pieces. Alternative methods, such as the Ångström method, monitoring the phase lag between the temperatures of a sinusoidally heated front face of a test-piece and the rear face, are more difficult to set up and may be less reliable. Amazouz et al. (1987) describe an in-plane method of determining thermal diffusivity which relies on radial heat flow in a thin sheet, but comment that accuracy is likely to be limited by the imprecision of the distance between two thermocouples on the rear sample face.

3.4 Thermal diffusivity measurement on composites

Taylor (1985) found that in testing coarse-grained refractory composite materials, reproducible measurements could be made only if the detector viewing area was significantly greater than the grain size. Inhomogeneity is a disadvantage for laser-flash type thermal diffusivity determinations on composite materials. Representative results are said to be achieved if the practical rule is used that the thickness of test-piece for through-thickness measurement should be at least four reinforcing units thick (e.g. at least four plies in a cross-ply laminate), and that the laser pulsed diameter at least four times the reinforcement repeat distance (i.e. at least four weaves of a woven laminate). Provided these criteria are met, the heat flow is averaged out over the area of transient detection, and the result is broadly representative of a larger piece of material. Balgeas (1984) and Pujola and Balgeas (1985) have analysed the likely situation for fibre-reinforced composites, and demonstrated that under transient heating conditions, the thermal wave passing through the test-piece is non-uniform, and the apparent thermal diffusivity can be controlled by the rate of lateral heat flow between matrix and reinforcement, and hence on the thermal resistance of the interface. Only by having sufficient units of microstructure does the local effect become smeared and a true average result can then be obtained. Taylor (1982), reiterated by Whittaker et al. (1990), demonstrated that for a composite the theoretical transient curve for a homogeneous material was not obtained unless the composite thickness is at least four plies thick allowing averaging of the response.

The scatter of results from sample to sample as a result of local material variation is likely to determine the limitation on overall potential error to be added to the basic uncertainty of measurement. The rule of thumb above probably gives results reliable to no better than about $\pm 10\%$.

Test-pieces for thermal diffusivity measurement, provided that they meet the criteria outlined above for the representative nature of the spatial arrangement of reinforcements relative to test-piece size, are generally straightforward to prepare, parallelism being the key requirement. As a rule, test-pieces need to be of sufficient thickness to avoid the need for excessive finite pulse time corrections, yet thin enough to ensure that radiation losses occurring with a long $t_{1/2}$ time are not excessive, and that heat losses from the sides of the test-piece are acceptably low. Typically, a low thermal conductivity material ($< 1 \text{ W m}^{-1}\text{K}^{-1}$) will require a thickness of about 1 mm, while for a high conductivity material ($> 50 \text{ W m}^{-1}\text{K}^{-1}$) will require a thickness of about 3 mm. These dimensions are appropriate for most types of composite, although some of those with coarse weaves may not meet the homogeneity requirements described above for some measurement facilities designed for small test-piece diameters.

3.5 Thermal conductivity modelling

Most modelling has been done using thermal conductivity rather than thermal diffusivity as the material characteristic in order to simplify the task to one of a uniform stationary temperature distribution. There are various models for the net thermal conductivity of dispersed phase bodies. These models have been reviewed by Taylor (1991), and specifically for fibre composites, by Mottram and Taylor (1991). For present purposes there are three geometries of interest, those of dispersed spheres, dispersed platelets and aligned fibres, the last of these being the solution for infinite cylinders. All models start with assumptions concerning the geometry of the array of reinforcement.

Definitions

For the purposes of this section, the following symbols are used:

λ_{eff}	=	Effective thermal conductivity of composite in specified direction (subscripts t and l are for directions respectively transverse and longitudinal to defined directions, e.g. fibre axis)
λ_r	=	Thermal conductivity of reinforcing phase in specified direction
λ_m	=	Thermal conductivity of matrix phase
h	=	Thermal conductance of interface between reinforcement and matrix
l	=	Representative dimension of reinforcement = radius or spherical particle or fibre = half-thickness of plate
r	=	Radial variable
T	=	Temperature variable
V_r	=	Volume fraction of reinforcement
V_m	=	Volume fraction of matrix ($V_r + V_m = 1$)

Models for spherical particle reinforcement

Maxwell's (1892) solution (originally for electric currents) is based on the temperature distribution for a spherical particle inside a cube of matrix under "dilute" conditions yields the equation:

$$\frac{\lambda_{eff}}{\lambda_m} = \frac{\lambda_r + 2\lambda_m - 2V_r(\lambda_m - \lambda_r)}{\lambda_r + 2\lambda_m + V_r(\lambda_m - \lambda_r)} \quad (17)$$

where for $\lambda_m < \lambda_r$, λ_{eff} increases with increasing V_r , and for $\lambda_m > \lambda_r$, λ_{eff} decreases with increasing V_r . Rayleigh (1892) produced the same equation for electrical conductivity, and extended it for the non-dilute case. Others have modified this equation to take account of thermal interactions between the reinforcing particles. All these formulations assume that there is perfect heat transfer between the matrix and the dispersed phase. In composite materials this is clearly not always the case, so Hasselman and Johnson (1987) have taken thermal resistance of the interface into account, and have solved the Laplace equation with modified boundary conditions at the interface, namely that:

$$T_r - T_m = -(\lambda_r/h)(\partial T/\partial r) \quad (18)$$

where r is the radial direction. Their solution for dilute dispersions is:

$$\frac{\lambda_r}{\lambda_m} = \frac{2V_r \left(\frac{\lambda_r}{\lambda_m} - \frac{\lambda_r}{lh} - 1 \right) + \frac{\lambda_r}{\lambda_m} + \frac{2\lambda_r}{lh} + 2}{V_r \left(\frac{\lambda_r}{\lambda_m} + \frac{\lambda_r}{lh} \right) + \frac{\lambda_r}{\lambda_m} + \frac{2\lambda_m}{lh} + 2} \quad (19)$$

It can be deduced that when the conductance of the interface is infinite (perfect thermal

contact) this equation reduces to the Maxwell equation (3). As the value of lh becomes very much less than λ_m or λ_r , terms in λ_r/lh dominate, the expression reduces to:

$$\frac{\lambda_{eff}}{\lambda_m} = \frac{1 - 2V_r}{1 + V_r}$$

which is the Maxwell equation with the reinforcement thermal conductivity λ_r set to zero. Equation 19 is illustrated by Figure 3 for $\lambda_r/\lambda_m = 10$ (i.e. high conductivity reinforcement, low conductivity matrix), and shows how thermal conductivity changes with V_r . The result is very sensitive to changing interface conductance. For $\lambda_r/\lambda_m = 0.1$ (i.e. low conductivity reinforcement, high conductivity matrix), the sensitivity to changes in λ_r/ah is much reduced, although the sensitivity to V_r increases. Clearly the changes delineated in Figure 3 represent extremes of behaviour, and it is unlikely in most particulate composites that microstructural changes would be sufficiently extensive to make such marked changes.

3.5.3 Models for platelet reinforcement

Bruggeman (1935) generalised Maxwell's formulation to the case of orientated ellipsoids and produced the equation:

$$-V_r = \left[\frac{\lambda_r - \lambda_{eff}}{\lambda_r - \lambda_m} \right] \left[\frac{\lambda_m}{\lambda_{eff}} \right]^{1/\beta + 1} \quad \text{where } \beta = \frac{(1/Y + 1/Z)}{R/X}$$

where β is a shape factor derived from the ellipsoidal axes X parallel to the heat flow, and Y and Z perpendicular to the heat flow, and R is a roughness factor (≈ 1). This approach should be considered as an approximation to platelet geometry. Hasselman and Johnson (1987) used a different approach of a series of thermal resistances for platelets of half-thickness a to take account also of interface resistance to give the formula:

$$\frac{\lambda_{eff}}{\lambda_m} = \frac{1}{V_r \left(\frac{\lambda_r}{\lambda_m} + 2 \frac{\lambda_r}{ah} + \frac{\lambda_r}{\lambda_m} \right)}$$

For $h \rightarrow \infty$, this relationship reduces to:

$$\frac{1}{\lambda_{eff}} = \frac{V_r}{\lambda_r} + \frac{V_m}{\lambda_m}$$

which is the same as that for a simple series model with perfect contact resistance.

3.5.4 Models for fibre reinforcement

For heat flow parallel to unidirectional continuous fibres, it is usual to assume parallel thermal resistances giving a rule of mixtures type formula:

$$\lambda_{eff,l} = \lambda_{r,l} V_r + \lambda_m V_m \quad (24)$$

In this case, the fibre/matrix interface plays no role in the behaviour since heat flow is always parallel to and not perpendicular to the interface. For heat flow perpendicular to fibres, a series thermal resistance model gives:

$$\frac{1}{\lambda_{eff,t}} = \frac{V_r}{\lambda_{r,t}} + \frac{V_m}{\lambda_m}$$

Note that the fibre thermal conductivity has been assumed to be anisotropic. Alternatively, Equation 21 reduces for the case of $\beta = 1$, giving a different formula with numerically different results.

This theory is simplistic, and takes no account of interactions between adjacent fibres. As for the effective bulk modulus described above, Hashin and Shtrikman (1963) have approached the modelling by a variational method, providing upper and lower second order bounds to the solution, initially for spheres, and later by Hashin (1983) for fibrous structures. In the form given by Taylor and Mottram (1991):

$$\lambda_{eff,t}^{(-)} < \lambda_{eff,t} < \lambda_{eff,t}^{(+)}$$

where:

$$\frac{\lambda_{eff,t}^{(-)}}{\lambda_f} = \frac{1 + (d - 1)V_r\beta_{21}}{1 - V_r\beta_{21}}$$

$$\frac{\lambda_{eff,t}^{(+)}}{\lambda_f} = \frac{1 + (d - 1)V_m\beta_{12}}{1 - V_m\beta_{12}}$$

where:

$$d = 2 \text{ for fibres, } \beta_{ij} = \frac{\lambda_i - \lambda_j}{\lambda_i + (d - 1)\lambda_j}, \quad i \neq j$$

Extension of the concept to more precise bounds have been made by a number of other authors with special concern for transverse conductivity in fibrous composites. These are reviewed in detail in Mottram and Taylor (1991).

For the direction perpendicular to fibres, Hasselman and Johnson (1987) used the same boundary condition as in Equation 18 to solve for the case of finite interface heat flow resistance, and derived:

$$\frac{\lambda_{eff,t}}{\lambda_m} = \frac{V_r \left(\frac{\lambda_r}{\lambda_m} - 1 - \frac{\lambda_r}{lh} \right) + 1 + \frac{\lambda_r}{lh} + \frac{\lambda_r}{\lambda_m}}{V_r \left(\frac{\lambda_r}{\lambda_m} - 1 - \frac{\lambda_r}{lh} \right) + 1 + \frac{\lambda_r}{lh} + \frac{\lambda_r}{\lambda_m}}$$

which for $h \rightarrow \infty$ reduces to Rayleigh's (1892) solution (originally for electrical conductivity):

$$\frac{\lambda_{eff,t}}{\lambda_m} = \frac{\lambda_m(1 - V_r) + \lambda_r(1 + V_r)}{\lambda_m(1 + V_r) + \lambda_r(1 - V_r)}$$

Evaluation of Equation 31 for $\lambda_r/\lambda_m = 0.1, 1$ and 10 is given in Figure 4. In these figures it becomes clear that for a given volume fraction of reinforcement, the thermal conductivity of the composite is most sensitive to change of interfacial conductance when the thermal conductivity of the fibre is much higher than that of the matrix. If the thermal conductivities are similar, the high sensitivity only applies when λ_r/lh is small, < 10 , i.e. for high interface conductance. If the thermal conductivity of the fibre is lower than that of the matrix, the interface is of little significance, and thus changes in interface conductance have little effect on overall thermal conductivity. Similar formulations for particulate reinforcements have been studied by Benevise and Miloh (1986), Benevise (1987) and Benevise and Miloh (1992).

Hatta and Taya (1985, 1986) have extended the theory to the case of prolate spheroids approximating to short fibres, additionally with a coating. The complex numerical solutions to the equations derived are dependent on the coating thickness and its thermal conductivity relative to the reinforcement, with the maximum effect occurring when the coating has poor thermal conductivity, as would be expected.

3.6 Experimental results

There is a large literature relating measurements to models, with varying degrees of success. A common theme is that it is usually necessary to explain some deviations from models in terms of details of microstructure, or to changes in microstructure occurring during measurement. It is impossible to review the entire literature, so below are summarised some examples, concentrating on instances where significant changes to thermal transport parameters have been found.

3.6.1 As-produced materials

Russell et al. (1987) examined the thermal diffusivity as a function of temperature for two forms of SiC whisker added as a reinforcement to a mullite matrix, and were able to use models to demonstrate that different whisker types had greatly different thermal conductivities. They later (Russell et al. (1991)) performed a similar examination for the same whiskers added as reinforcement to hot-pressed or HIPed Si_3N_4 matrices, with similar conclusions. Modelling of thermal conductivity as a function of whisker volume fraction demonstrated a departure from that expected, explained by hypothesising that there was an increasing risk of whisker fracture in hot-pressing, reducing the thermal conductivity.

Bhatt et al. (1990, 1992) have used the interfacial thermal conductance model described above

to study the interfaces in carbon coated large-diameter carbon cored SiC fibres (Textron SCS) reinforcing reaction bonded Si_3N_4 before and after HIPing to improve matrix density. By undertaking measurements of thermal diffusivity in different gas atmospheres and in vacuum they were able to demonstrate that the interface gap due to transverse thermal expansion mismatch was sufficiently large below 800 °C for the atmosphere to penetrate and control the net transverse conductivity. At higher temperatures the interfacial gap closed, and thermal conductivity became independent of measurement atmosphere.

Amongst several authors, Taylor (1985) reports the effect of measurement atmosphere on thermal diffusivity, for the case of carbon/carbon composites. This arises because the atmosphere has direct access to pores or reinforcement/matrix interfaces, and changes the local heat transfer coefficient. Often it is found that the lowest thermal diffusivity is obtained in vacuum, and the highest in helium.

3.6.2 Materials suffering thermal degradation

Particulate reinforcement

A study of thermal diffusivity in Ti-10% SiC_p and Ti-10, 20% TiB_{2p} composite MMCs has shown that whereas TiB_2 as reinforcement produces little if any reaction zone, and maintains good thermal contact, and hence a composite thermal diffusivity close to what would be expected by the rule of mixtures, there is much more marked reaction with SiC, forming TiC and Ti_3Si_5 (Turner et al. (1993)). The authors note that the interfacial reaction is accompanied by a volume change of about -4.6%, and the brittle character of the resulting interface allows interfacial cracking. The poor thermal conductance associated with the damaged interface reduces the thermal conductivity by about 10% compared with Ti itself, instead of increasing it by 30%, as might be modelled. Continued heat treatment at 950 °C dramatically worsens the situation. In contrast, extended heat treatment of the Ti- TiB_{2p} composite changed the thermal conductivity relatively little, despite some reaction to the monoboride, TiB. The authors conclude that the microcracking associated with the brittle reaction products in the SiC_p case was the cause of the major changes.

Fibre reinforcement

Hasselman et al. (1987) found that the thermal diffusivity of a carbon fibre/low thermal expansion spodumene glass-ceramic matrix composite suffered hysteresis on heating and cooling, and even at 300 °C was time dependent. In view of the substantial thermal mismatch between the transverse expansion coefficient of carbon fibre and the matrix, interfaces were cracked, but tended to heal on reheating to 800 °C and above. The second and subsequent thermal cycles gave apparently consistent results.

Johnson et al. (1987) studied the thermal diffusivity of carbon fibre/borosilicate glass composite, and found that permanent decreases of 5-10% took place on heating above 600 °C. They postulated that the original hot-pressing process resulted in mechanically strained fibres, and heating above the annealing temperature of the glass allowed this strain to relax, opening microstructurally visible interfacial gaps which were larger than those due to the likely transverse thermal expansion mismatch between glass and fibre.

Whittaker et al. (1990) demonstrate the effects of permanent graphitisation changes in carbon/carbon composites during heating to obtain thermal diffusivity measurements, resulting in a measureable increase in thermal diffusivity on subsequent cooling. These

authors also examined the effect of residual porosity from processing, both in the form of tubular pores parallel to fibres, and arc-shaped pores within the CVD deposited carbon around fibres, using the developed theory to provide a reasonable match with experimental results.

Hasselman et al. (1991A) have shown that for a unidirectional CVI SiC/SiC_f, heating to 1500 °C has resulted in an increase in thermal diffusivity parallel to the fibres of about 10% from the as-manufactured results following crystallisation of the fibres, which has the effect of raising their intrinsic thermal conductivity. However, perpendicular to the fibres, the diffusivity measured in air fell by typically 30%, and became sensitive to the test atmosphere as a result of interfacial debonding and matrix cracking occurring on heating above the original fabrication temperature. This is in contrast to previous results obtained on material annealed at 1800 °C where no effect was found (Tawil et al. (1985)), this being explained by the greater ability to anneal internal stress due to crystalline anisotropy at very high temperatures. Similar behaviour has also been found for alumina fibre reinforced CVI SiC matrix material (Hasselman et al (1991B)) in which the greater thermal expansion of alumina than silicon carbide on heating above the original fabrication temperature causes matrix cracking and interfacial delamination, leading to a permanent reduction of thermal diffusivity when measured in nitrogen, and to an atmosphere dependence of the results.

Taylor and Piddock (1989) measured the transverse thermal diffusivity of a carbon fibre/silicon carbide matrix composite with a quasi-isotropic, multi-ply 0°, 60°, 120° fibre architecture plus about 20% of the fibres perpendicular to this plane giving a pseudo-three-dimensional structure. Although the material already possessed matrix cracks in the as-received condition, they found a small permanent reduction in thermal diffusivity following heating above about 1200 °C, attributed to small changes in structure resulting from heating above the original fabrication temperature (1000 °C).

Gordon et al. (1994) compared thermal diffusivity behaviour obtained in an earlier study (Turner et al. (1993)) of particulate reinforcement of Ti by SiC particles with that in Ti-6Al-4V alloy and continuous SiC monofilament reinforcement. In the latter case, although similar reactions took place, the total number of interfaces in the transverse direction was much smaller because of the scale of the reinforcement, leading to less influence on thermal diffusivity, but none-the-less significantly lower than expected by the rule of mixtures approach. Using the Hasselman and Johnson (1987) approach to interfacial conductance, this parameter was estimated at about $10^6 \text{ W m}^{-2} \text{ K}^{-1}$, decreasing with decreasing temperature. Similar conclusions were deduced from measurements on a short-fibre extruded Ti-10% SiC_f composite.

3.7 Conclusions

From the above discussion it is clear that thermal conductivity/diffusivity measurements are a potentially sensitive tool for determining changes in composites resulting from microstructural degradation. This arises from the effect on composite thermal conductivity of changes in interfacial thermal conductance, which is very sensitive to interfacial delamination or progressive development of microcracks. Note, however, that if the reinforcing phase has a thermal conductivity much less than that of the matrix, changes in the interface have little influence on the heat flow, which takes place predominantly in the matrix around the reinforcement, rather than across interfaces. For high-conductivity reinforcements, the possibility of non-destructive methods of determining thermal conductivity/diffusivity, such as hot probe methods, either through thickness or in plane,

makes it feasible in principle to examine components. If it were possible to correlate thermal conductivity/ thermal diffusivity with residual mechanical properties after a given service period, in principle the remaining life might be determined.

4. SPECIFIC HEAT

4.1 Specific heat measurement

Using one of the several differential scanning calorimetry techniques, specific heat can generally be determined to an accuracy of about $\pm 1\%$ over the temperature range -50 to 700 °C. The reference material is usually α -alumina. The sample may be solid material provided this can be shaped adequately to fill the specimen holder, but may with advantage be powdered. With particular regard to composites, as with thermal diffusivity attention needs to be given to the representative nature of the small sample if the composite is textured in any way.

Other techniques are normally required at higher temperatures because the accuracy of DSC techniques declines due to thermal noise. Drop calorimetry, with an accuracy of typically $\pm 5\%$ is effective at higher temperatures, although a more-specialised measurement. Using a series of drops from different temperatures, the specific heat is derived from the enthalpy determinations by curve-fitting and differentiation.

4.2 Specific heat measurement on composites

The majority of materials pose no problems of measurement provided that the test-piece, which is normally quite small, is representative of the bulk material. Brittle materials can be readily ground to powder, and the well-mixed powder sampled. However, for metal-matrix materials this is not possible, and measurement relies on shaping an appropriate disc-shaped test-piece from solid. It would be a wise precaution to test several test-pieces if there is a risk of non-representative structure with the small test-piece size.

4.3 Modelling of specific heat

Specific heat (heat content per unit mass) values are functions of temperature, and to a first approximation are determined by the proportions of the atomic species in each of the phases present in the material. The actual crystalline structure of the material plays a secondary role. In addition, phase transformations not only have an associated heat of transformation, but the change in structure may change the instantaneous specific heat. An additional aspect is mechanical constraint (removed if the sample is ground to powder!). As demonstrated by Budiansky (1970) for an isotropic material, the specific heat at constant pressure, C_p (i.e. freely expanding), is greater than that at constant volume, C_v by a factor determined by bulk modulus (K), bulk expansivity (β) and temperature (T):

$$C_p = C_v + K\beta^2 T \quad (32)$$

This applies also to isotropic composites where the parameters refer to composite properties. The second term is usually negligible (Budiansky (1970)), and thus, somewhat unfortunately, changes due to small alterations in composition or in the degree of internal elastic constraint

in composites is not likely to be readily measurable. In a more detailed analysis, upper and lower bounds on specific heat have been estimated by Rosen and Hashin (1970).

4.4 Measurements of specific heat

Detailed data are not frequently reported, despite the need often to convert thermal diffusivity data to thermal conductivity.

Of course, the question should be asked as to whether specific heat of composites actually needs to be measured, or whether it can simply be modelled with adequate accuracy from thermodynamic data of the component materials. To a first approximation estimation is probably perfectly adequate. It is also often the case that there are no significant changes to specific heat as a result of the small changes following from changes in interfacial phase types or proportions. However, in some cases significant changes can occur.

Some of the largest changes observed have been in carbon/carbon materials as a result of changes in the crystallinity of both matrix and fibres following exposure to very high temperatures. Changes of up to 25% have been reported by Tanabe et al. (1987) following heat treatments at temperatures between 1000 and 3000 °C. This type of change is clearly of great significance in the calculation of engineering performance, but is unusual for composite materials.

5. SUMMARY OF DISCUSSION OF THEORETICAL MODELS AND SENSITIVITY TO CHANGES IN MICROSTRUCTURE WITH THERMAL EXPOSURE

A summary of the perceived position regarding thermal property measurements for composites is given in Table 2.

It is fairly clear from the above discussion that the theoretical aspects of modelling both thermal expansion and thermal conductivity are fairly well developed for different composite architectures. They are becoming progressively more sophisticated in the sense that the effects of reinforcement architecture can be taken into account. In many cases of well-behaved materials, the thermal expansion and thermal conductivity/diffusivity behaviours of manufactured composites match reasonably well with model predictions. Some of the models showing reasonable experimental fits are summarised in Table 3, with the caveat that it remains difficult to be certain of the more-general validity of these fits.

The majority of simple models for thermal properties of composites are based on a number of assumptions which are not always valid in practice. For example it may be assumed that the thermal and mechanical properties of both fibres and matrix are isotropic and homogeneous. In many practical situations this is not the case, and progressively more sophisticated models are required to take such factors into account. Assumptions are also made concerning the interface between the matrix and reinforcement.

In the case of thermal expansion, the internal stresses in the composite are an important factor in determining overall thermal expansion behaviour as a consequence of thermal expansion mismatch and Poisson contract/expansion effects in matrices constrained by reinforcements. The usual assumption is either that the interface is mechanically intact, and that all stresses are transferred across the interface, or that only a part of the interface (e.g. in the short-fibre shear lag model) supports the stresses. In practice, interfaces may support

stress if these are radially compressive, but not if they are radially tensile. These factors make modelling difficult, and results tend to be sensitive to factors which are difficult to measure directly, such as transverse properties of fibres. If additionally, the matrix is capable of stress relaxation within the timescale of observation, this will not only lead to permanent size changes, but possibly also to short-term thermal expansion behaviour. Thermal expansion hysteresis is complex and, if present, provides some pointers to features such as temperatures of onset of internal stress build-up, but is not simple to analyse. Thus while thermal expansion measurements are a very important feature of the design and interpretation of composite materials, especially in the case of complex systems in which the basic composite modelling assumptions are not upheld, they cannot necessarily be sufficiently well modelled to allow the inverse interpretation of the significance of small changes that might signify thermal degradation.

In the case of thermal conductivity/thermal diffusivity behaviour, the modelling aspect is more straightforward, and does not depend directly on a complex mechanical interaction, but solely on the heat flow path. In this sense, although similar assumptions of isotropic thermal conductivity behaviour are often made, but not always justifiable, in modelling, rules of mixtures for perfectly conducting interfaces provide good matches to practical observations. There has additionally been some progress in the last decade towards defining models with interfacial thermal resistance, so that changes in thermal conductivity/thermal diffusivity resulting from changes in interfaces caused by mechanical or thermal degradation can now be understood. Furthermore, as noted by a number of authors, the use of such models can now offer the potential for a non-destructive determination of potential material degradation in service. Laboratory methods of thermal diffusivity determination could in principle be developed to cope with components rather than small test-pieces cut from them. The absolute accuracy, usually not better than about $\pm 5\%$, is not a critical feature when one is looking for changes.

Specific heat is determined by the type and amount of the phases present. Second order effects are due to internal stresses and annealing effects. Composite materials can therefore be modelled to some extent, but with only a few exceptions, specific heat measurements are less sensitive to thermally induced changes in materials than thermal expansion or thermal conductivity measurements.

In conclusion, thermal conductivity/thermal diffusivity measurements potentially offers the best tool for diagnostic investigation of changes in composite materials brought about by service conditions. There are possibilities of determining such changes non-destructively on components rather than on carefully prepared test-pieces as usually required by the other techniques. Although it would be necessary to understand the relationship between unacceptable loss of mechanical integrity and changes in thermal conductivity/thermal diffusivity for each particular material, once this had been done it would be straightforward to provide a pass/fail criterion for composite degradation.

Acknowledgement

The author would like to thank the considerable assistance of Prof. Roy Taylor of the Materials Science Centre, UMIST, and of colleagues at NPL, for advice in the preparation of this review. This work is part of a programme sponsored by EED Division of the Department of Trade and Industry under the Design of Composite Components programme (1993-6).

References

- Amazouz, M., Moyne, C., Degiovanni, A. (1987). "Measurement of the thermal diffusivity of anisotropic materials", *High Temp. - High Press.* **19** 37-41.
- Balgeas, D.L. (1984). "Détermination par la méthode flash des propriétés thermiques des constituants d'un composite à renforcement orienté", *High Temp. - High Press.* **16** 199-208.
- Benevise, Y. (1987). "Effective thermal conductivity of composites with thermal contact resistance between the constituents, non-dilute case", *J. Appl. Phys.* **61** 2840-3.
- Benevise, Y., Miloh, T. (1987). "The effective thermal conductivity of composites with imperfect thermal contact at constituent interfaces", *Int. J. Engg. Sci.* **24** 1537-52.
- Benevise, Y., Miloh, T. (1991). "On the effective thermal conductivity of coated short-fiber composites", *J. Appl. Phys.* **69** 1337-44.
- Bhatt, H., Donaldson, K.Y., Hasselman, D.P.H. (1990). "Role of the interfacial thermal barrier in the effective thermal diffusivity/conductivity of SiC-fiber-reinforced Reaction-bonded silicon nitride", *J. Amer. Ceram. Soc.* **73**(2) 312-6.
- Bhatt, H., Donaldson, K.Y., Hasselman, D.P.H., Bhatt, R.T. (1990). "Effect of Hipping on the effective thermal conductivity/diffusivity and the interfacial conductance of uniaxial SiC fibre-reinforced RBSN", *J. Mater. Sci.* **27** 6653-61; see also same authors, *Thermal conductivity 21*, edited by Cremers, C.J., Fine, H.A., Plenum Press, New York, pp 597-609.
- Bruggemann, D.A.G. (1935). "Dielectric constant and conductivity of mixtures of isotropic materials". *Ann. der Physik (Leipzig)* **24** 636-79.
- Budiansky, B (1970). "Thermal and thermoelastic properties of isotropic composites", *J. Compos. Mater.* **4**(7) 286-95.
- Clyne, T.W., Withers, P. J. (1993). *An introduction to metal matrix composites*, Cambridge University Press, Cambridge, UK.
- Daehn, G.S., Gonzalez-Doncel, G. (1989). "Deformation of whisker-reinforced metal-matrix composites under changing temperature conditions", *Metall. Trans.* **20A**(11) 2355-68.
- Douglas, F.C.; Prewo, K.M. (1983). "Differential thermal expansion studies of graphite reinforced glass matrix composites", in *Thermal expansion 7*, edited by Larsen, D.C., Plenum Press, New York, USA, 89-102.
- Eckel, A.J., Bradt, R.C. (1990). "Thermal expansion of laminated, woven continuous ceramic fiber/chemical-vapor-infiltrated silicon carbide matrix composites", *J. Amer. Ceram. Soc.* **73**(5) 1334-8.
- Elkind, A.; Barsoum, M.; Kangutkar, P. (1992). "Thermal expansion of silicon carbide monofilaments and silicon carbide-borosilicate composites", *J. Amer. Ceram. Soc.* **75**(10) 2871-3.

- Eshelby, J.D. (1957). "The determination of the elastic field of an ellipsoidal inclusion and related problems", *Proc. Roy. Soc.* **A241** 377-96.
- Eshelby, J.D. (1959). "The elastic field outside an elliptical inclusion", *Proc. Roy. Soc.* **A252** 561-9.
- Gordon, F.H., Turner, S.P., Taylor, R., Clyne, T.W. (1994). "The effect of the interface on the thermal conductivity of titanium-based composites", *Composites* **25**(7) 583-91.
- Hancox, N.L., McCartney, L.N. (1990). "Critical appraisal of micromechanical and continuum methods of predicting the effects of damage and defects in composite materials", IACFA Report, National Physical Laboratory, Teddington, UK.
- Hashin, Z. (1983). "Analysis of composite materials - a survey", *J. Appl. Mech.* **50**(9) 481-505.
- Hashin, Z., Shtrikman, S. (1963). "A variational approach to the theory of the elastic behaviour of multiphase materials", *J. Mech. Phys. Solids* **11** 127-140.
- Hasselman, D.P.H., Johnson, L.F. (1987). "Effective thermal conductivity of composites with interfacial thermal barrier resistance", *J. Compos. Mater.* **21**(6) 508-15; see also same authors *Cer. Eng. Sci. Proc.* **7** (1986) 1011-3.
- Hasselman, D.P.H., Johnson, L.F., Syed, R., Taylor, M.P., Chyung, K. (1987). "Heat conduction characteristics of a carbon-fibre-reinforced lithia-alumino-silicate glass-ceramic", *J. Mater. Sci.* **22** 701-9; see also Hasselman, D.P.H. (1988). "Compositional and structural effects on the thermal diffusivity of fiber-reinforced glass-ceramic and ceramic matrix composites", *Thermal conductivity 19*, edited by Yarborough, D.W., Plenum press, New York, pp 388-402..
- Hasselman, D.P.H., Venkateswaran, A., Yu, M., Tawil, H. (1991A). "Role of interfacial debonding and matrix cracking in the effective thermal diffusivity of SiC fibre-reinforced chemical vapour deposited SiC matrix composites" *J. Mater. Sci. Lett.* **10** 1037-42 (see also same authors, *Cer. Eng. Sci. Proc.* **12**(9-10) 2251-2261).
- Hasselman, D.P.H., Venkateswaran, A., Tawil, H. (1991B). "Role of interfacial debonding and matrix cracking in the effective thermal diffusivity of alumina-fiber-reinforced chemical-vapor-infiltrated silicon carbide matrix composites", *J. Amer. Ceram. Soc.* **74**(7) 1631-34.
- Hatta, H., Taya, M. (1985). "Effective thermal conductivity of a mis-orientated short-fiber composite", *J. Appl. Phys.* **58**(7) 2478-86.
- Hatta, H., Taya, M. (1986). "Thermal conductivity of coated filler composites", *J. Appl. Phys.* **59**(6) 1851-60.
- Hawkins, G.F., Wolff, E.G. (1983). "Isotropic zero CTE materials", in *Thermal expansion 7*, edited by Larsen, D.C., Plenum Press, New York, USA, 103-118.
- Johnson, L.F.; Hasselman, D.P.H., Minford, E. (1987). "Thermal diffusivity and conductivity of a carbon fibre-reinforced borosilicate glass", *J. Mater. Sci.* **22** 3111-7.

- Kehoe, F.P.; Chadwick, G.A. (1991). "Mechanical and physical properties of squeeze-cast aluminium metal matrix composites containing 5-30% Saffil", *Mater. Sci. Eng.* **A135** 209-12.
- Kreider, K.G., Patarini, V.M. (1970) "Thermal expansion of boron fiber - aluminum composites", *Metal. Trans.* **1** 3431-5.
- Kuszyk, J.A., Bradt, R.C. (1973). "Influence of grain size on effects of thermal expansion anisotropy in MgTiO_2 ", *J. Amer. Ceram. Soc.* **56**(8) 420-23.
- Ledbetter, H., Austin, M. (1991). "Thermal expansion of an SiC particle-reinforced aluminum composite", *Int. J. Thermophys.* **12**(4) 731-9.
- Levin, V.M. (1967). "On the coefficients of thermal expansion of heterogeneous materials", *Mech. Solids* **2** 58-61 (English translation from *Mekhanika Tverdogo Tela* **1** (1967) 88-94.).
- McCartney, L.N. (1992a). "An analytical method of calculating the thermoelastic constants of a multiphase unidirectional composite". NPL Report DMM(A)57.
- McCartney, L.N. (1992b). "Theory of stress transfer in a 0-90-0 cross-ply laminate containing a parallel array of transverse cracks". *J. Mech. Phys. Solids* **40** 27-68 .
- McCartney, L.N., Morrell, R. (1995). "Validation of models of thermal expansion coefficients for fibre reinforced titanium composites", in press.
- Marom, G., Gershon, B. (1975). "Interfacial bonding and thermal expansion of fibre-reinforced composites", *J. Adhesion* **7** 195-201.
- Marom, G., Weinberg, A. (1975). "The effect of fibre critical length on the thermal expansion of composites", *J. Mater. Sci.* **10** 1005-10.
- Masutti, D., Lentz, J.P., Delannay, F. (1990). "Measurement of internal stresses and of the temperature dependence of the matrix yield stress in metal matrix composites from thermal expansion curves". *J. Mater. Sci. Lett.* **9** 340-2.
- Maxwell, J.C. (1892). *A Treatise on Electricity and Magnetism*, Vol. 1, 3rd Edition, Oxford University Press, London, p440.
- Mochida, T.; Taya, M.; Lloyd, D.J. (1991). "Fracture of particles in a particle/metal matrix composite under plastic straining and its effect on the Young's modulus of the composite", *Mater. Trans., JIM* **32** 931-42.
- Morimoto, K.; Suzuki, T., Yosomiya, R. (1984). "Thermal conductivity and thermal expansion behaviour of glass fiber reinforced rigid polyurethane foam", *Polymer Eng. Sci.* **24**(12) 943-9. .
- Mottram, R.C.; Taylor, R. (1991). "Thermal transport properties", in *Int. Encyclopedia of Composites*, edited by Lee, S.M., VCH, New York, USA, pp 476-95.
- Ohya, Y., Nakagawa, Z., Hamano, K. (1987) "Grain boundary microcracking due to thermal expansion anisotropy in aluminium titanate", *J. Amer. Ceram. Soc.* **70**(8) C184-6.

- Pujolà, R.M., Balgeas, D.L. (. 1985). "Derniers développements de la méthode flash adaptée aux matériaux composites à renforcement orienté", *High Temp. - High Press.* **17** 623-32.
- Raghava, R.S. (1988). "Thermal expansion of organic and inorganic matrix composites: a review of theoretical and experimental studies", *Polym. Compos.* **9**(1) 1-11.
- Rayleigh, Lord (1892). "On the influence of obstacles arranged in rectangular order upon the properties of a medium", *Phil. Mag.* **34** 481-507.
- Reeves, A.J., Taylor, R., Clyne, T.W. (1991). "The effect of interfacial reaction on thermal properties of titanium reinforced with particulate SiC", *Mater. Sci. Eng.* **A141** 129-38.
- Rogers, K.F., Phillips, L.N., Lee, D.M.K., et al. (1977). "Thermal expansion of carbon fibre reinforced plastics, I Influence of fibre type and orientation", *J. Mater. Sci.* **12** 718- .
- Rojstaczer, S., Cohn, D., Marom, G. (1985). "Thermal expansion of Kevlar fibres and composites", *J. Mater. Sci. Lett* **4** 1233-6.
- Rosen, B.W., Hashin, Z. (1970). "Effective thermal expansion coefficients and specific heats of composite materials", *Int. J. Eng. Sci.* **8** 157-73.
- Russell, L.M., Johnson, L.F., Hasselman, D.P.H. (1987). "Thermal conductivity/diffusivity of silicon carbide reinforced mullite", *J. Amer. Ceram. Soc.* **70**(10) C226-C229.
- Russell, L.M., Donaldson, K.Y., Hasselman, D.P.H. et al. (1991). "Effect of vapour-liquid-solid and vapour-solid silicon carbide whiskers on the effective thermal diffusivity/conductivity of silicon nitride matrix composites", *J. Amer. Ceram. Soc.* **74**(4) 874-7.
- Schapery, R.A. (1968). "Thermal expansion coefficients of composite materials based on energy principles", *J. Compos. Mater.* **2**(3) 380-403.
- Scherer, G.W. (1987). "Use of a bimetal strip to predict expansion compatibility", *J. Dent. Res.* **66**(8) 1340.
- Sergo, V., Meriani, S. (1991) "Thermal expansion and percolation in a SiC whisker-reinforced ceramic composite", *J. Mater. Sci. Lett.* **10**(14) 855-7.
- Takahashi, K., Karakawa, K., Sakai, T. (1985). In: *Environmental effects on composite materials 2*, edited by Springer, G.S., Technomic Publishing Co., pp 348- .
- Takao, Y., Taya, M. (1987) "The effect of variable fibre aspect ratio on the stiffness and thermal expansion coefficients of a short fibre composite", *J. Compos. Mater.* **21**(2) 140-56.
- Tanabe, Y., Kimura, S., Yasuda, E. (1987). "Temperature dependence of thermal constants of carbon fiber/glass-like carbon composites", *Yogyo Kyokaishi* **95**(3) 341-4.
- Tandon, G.P., Chatterjee, A. (1991). "The transverse coefficient of thermal expansion of a unidirectional composite", *J. Mater. Sci.* **26** 2759-64.
- Tawil, H., Bentsen, L.D., Easkaran, S., Hasselman, D.P.H. (1985). "Thermal diffusivity of

- chemical vapour deposited silicon carbide reinforced with silicon carbide or carbon fibres", *J. Mater. Sci.* **20** 3201-12.
- Taylor, R. (1991). "Thermophysical Properties", in: *Int. Encyclopedia of Composites* Volume 6, edited by Lee, S.M., VCH, New York, USA, pp 530-48.
- Taylor, R., Piddock, V. (1989). "Thermal diffusivity of three-dimensionally reinforced carbon-fibre/silicon carbide matrix composites", *High Temp. - High Press.* **21** 97-104.
- Taylor, R.E. (1985). "Thermal diffusivity of heterogeneous materials", in *Thermal conductivity 19*, Proc. 19th Int. Conf. Thermal Conductivity, Cookville, TN, USA, edited by Yarborough, D.W., Plenum Press, NY, 1988, pp 403/12.
- Tummala, R.R., Friedberg, A.L. (1970). "Composites, carbides, thermal expansion of composite materials", *J. Appl. Phys.* **41**(13) 5104-7.)
- Turner, P.S. (1946). "Thermal-expansion stresses in reinforced plastics", *J. Res. Nat'l. Bur. Stand. (US)* **37** 239-50.
- Turner, S.P., Taylor, R., Gordon, F.H., Clyne, T.W. (1993). "Thermal conductivities of Ti-SiC and Ti-TiB₂ particulate composites", *J. Mater. Sci.* **28** 3969-76.
- Weissenbek, E., Rammerstorfer, F.G. (1993) "Influence of the fiber arrangement on the mechanical and thermo-mechanical behaviour of short-fiber reinforced MMCs. *Acta Metall. Mater.* **41**(10) 2833-43.
- Whittaker, A.J., Taylor, R., Tawil, H. (1990). "Thermal transport properties of carbon-carbon fibre composites, I: Thermal diffusivity measurements", *Proc. Roy. Soc. Lond. A.* **430** 167-81; "II: Microstructural characterisation", *ibid* **430** 183-97; "III: Mathematical modelling", *ibid* **430** 199-211.
- Xu, Z.R., Chawla, K.K., Mitra, R., Fine, M.E. (1994). Effect of particle size on the thermal expansion of TiC/Al XDTM composites", *Scripta Metall. Mater.* **31**(11) 1525-30.

Table 1 Design framework requirements for thermal properties of MMCs and CMCs

Material type	Thermal environment, typical					Shape tolerance, maximum permanent strain, %
	Maximum temperature, °C	Minimum temperature, °C	Number of life-time cycles required	Heating/cooling rates, K s ⁻¹	Exposure time/cycle, h	
MMCs Particulate or whisker reinforced	150-400	-50	> 5000 - 100,000	1 - 100	0.1 - 5	0.1?
Fibre reinforced	500	-50	> 50,000	~ 100 hot, ~ 10 cold	~ 1	0.1?
CMCs Particulate or whisker reinforced	1200	-50	>> 100,000	?	?	0.1?
Fibre-reinforced	1500+	-50	> 4000	~ 200	?	0.1?

Table 2 - Availability of thermal property measurement methods for design

Material type	Measurement method (I = in place, R = research needed)													
	Thermal expansion						Thermal conductivity			Thermal diffusivity				
	Laboratory method		Uncertainty		In-situ methods		Lab. Method	Uncertainty	In-situ methods	Laboratory methods		Uncertainty		In-situ methods
	Slow	Fast	Slow	Fast	Slow	Fast	Slow	Slow	Fast	Laser	Angstrom	Laser (1)	Angstrom	
MMCs Particulate or whisker reinforced	I	R	1%	?	I?	R	I	5%	I?	I	I	5%	5%?	R
Fibre reinforced: in-plane through-thickness	I	R	1%	?	R	R	R	20%	R	I	n/a	10%	n/a	R
	R	R	5%	?	R	R	R	20%	R	I	I	5%	5%?	R
CMCs Particulate or whisker reinforced	I	R	1%	?	R	?	I	5%	I?	I	I	5%	5%?	R
Fibre reinforced: in-plane through-thickness	I	R	1%	?	R	?	R	20%	R	I	n/a	10%	n/a	R
	R	R	5%	?	R	?	R	20%	R	I	I	5%	5%?	R

Key: (1) Uncertainties may be larger if material is not homogenous on scale of size of test-piece.

Table 3 - Some recommended models for thermophysical property estimation

Material type	Thermal expansion models	Thermal conductivity models
Particulate reinforced: spheres low volume fractions high volume fractions platelets whiskers	Bulk modulus modified ROM (Turner (1946), Schapery (1968)), thermomechanical (Eshelby (1957, 1959)) Upper and lower bound concepts (Hashin/Shtrikman (1963)) Schapery (1968) Schapery (1968)	Dilute suspension (Maxwell (1882)); interactive suspension (Rayleigh (1892)); interfacial conductance (Hasselman/Johnson (1987)) Bruggeman (1935) Bruggeman (1935)
Fibre reinforced: unidirectional: parallel through-thickness crossply: in-plane through-thickness random short fibres: in-plane through thickness	Levin (1967) Levin (1967) McCartney (1995) McCartney (1995) Levin (1967), Craft/Christensen (1981) Levin (1967), Craft/Christensen (1981)	Parallel rule of mixtures Series rule of mixtures; interfacial conductance (Hasselman/Johnson (1987)) Interfacial conductance (Hasselman/Johnson (1987)) Interfacial conductance (Hasselman/Johnson (1987))

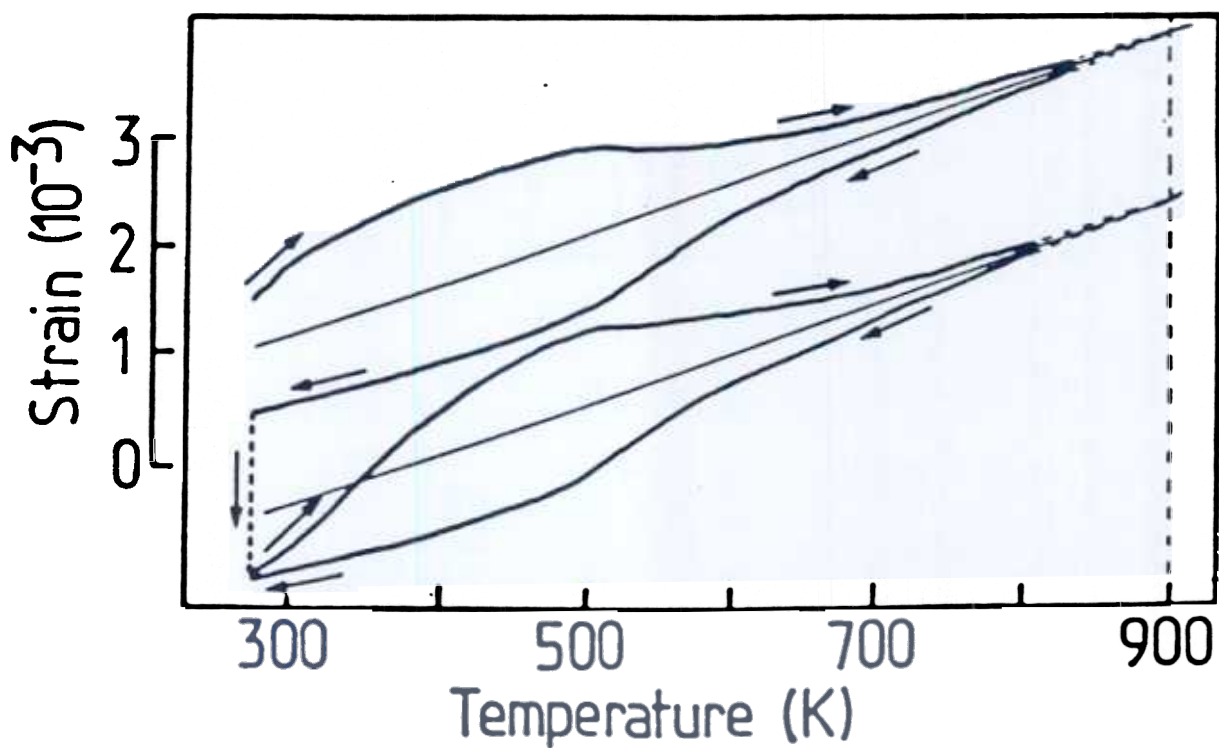


Figure 1 Thermal expansion hysteresis in an Al-3% MgO/30% SiC_f composite recorded in two thermal cycles after cooling the sample down to liquid nitrogen temperature (after Masutti et al. (1990).) (Reproduced by kind permission of the authors and Chapman and Hall Ltd from Figure 2 in Masutti, D., Lentz, J.P., Delannay, F. (1990). "Measurement of internal stresses and of the temperature dependence of the matrix yield stress in metal matrix composites from thermal expansion curves". J. Mater. Sci. Lett. 9 340-2.)

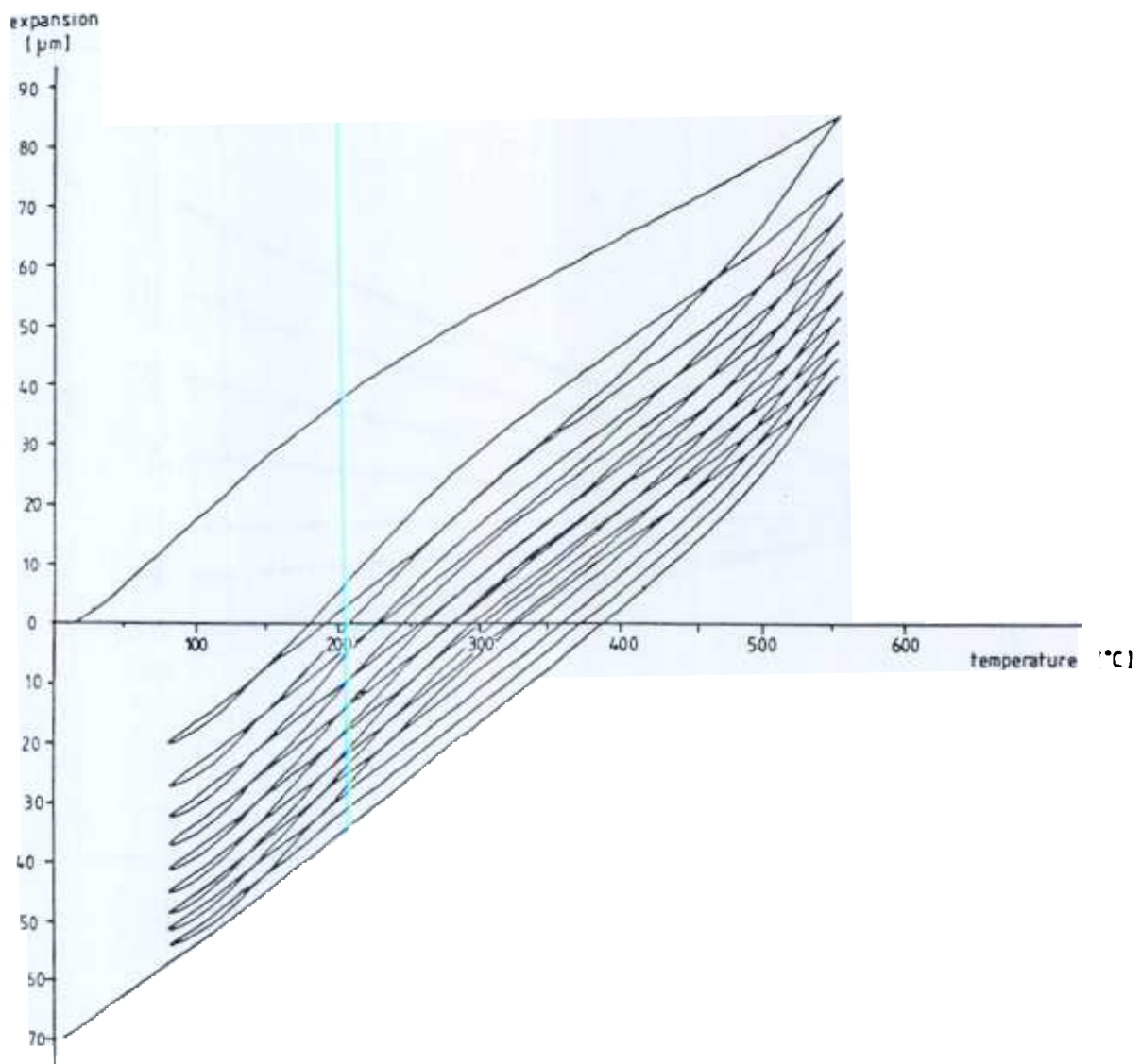


Figure 2 Progressive shrinkage on thermal cycling an Aluminium /15% Saffil fibre reinforced MMC. The degree of shrinkage decays with increasing number of cycles. (After Kehoe and Chadwick (1991).)

(Reproduced by kind permission of Elsevier Science Publishers SA, Lausanne, Switzerland, from Figure 3 in Kehoe, F.P., Chadwick, G.A., "Mechanical and physical properties of squeeze cast aluminium metal matrix composites containing 5%-30% Saffil", *Materials Science and Engineering A135* [1991] 209-12.)

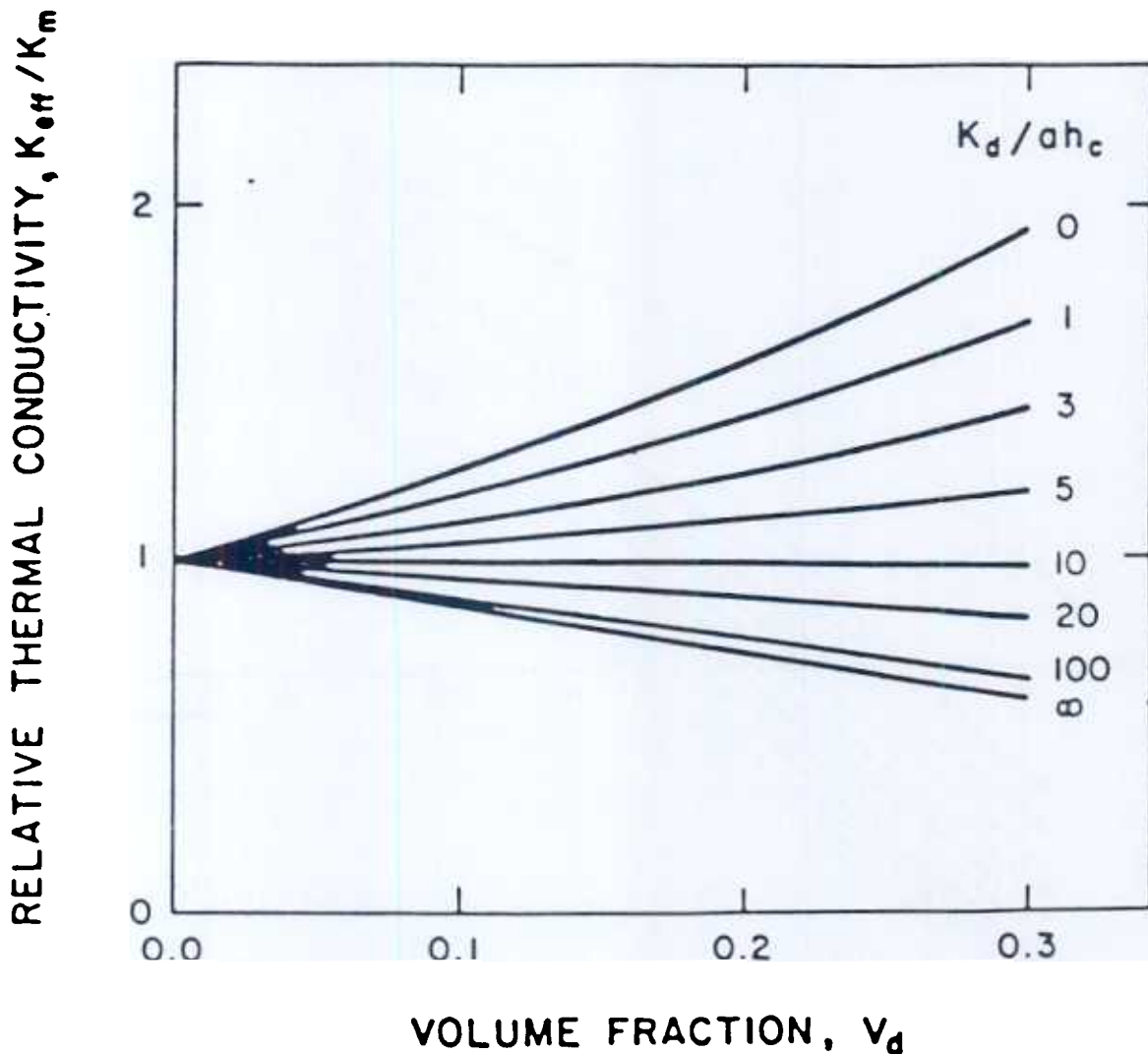


Figure 3 Effective thermal conductivity of matrix with spherical dispersions for $\lambda_r/\lambda_m = 10$, and for a range of values of the non-dimensional parameter λ_d/lh where h is the thermal conductance of the interface between matrix and reinforcement. Small changes to h can make a large relative change in thermal conductivity, especially for high volume fractions. (After Hasselman and Johnson (1987).)

(Reproduced by kind permission of the author and Technomic Publishing Co., PA, USA, from Figure 1 in Hasselman, D.P.H., Johnson, L.J., "Effective thermal conductivity of composites with interfacial thermal barrier resistance", J. Composite Materials, 21 [1987] 508-15.)

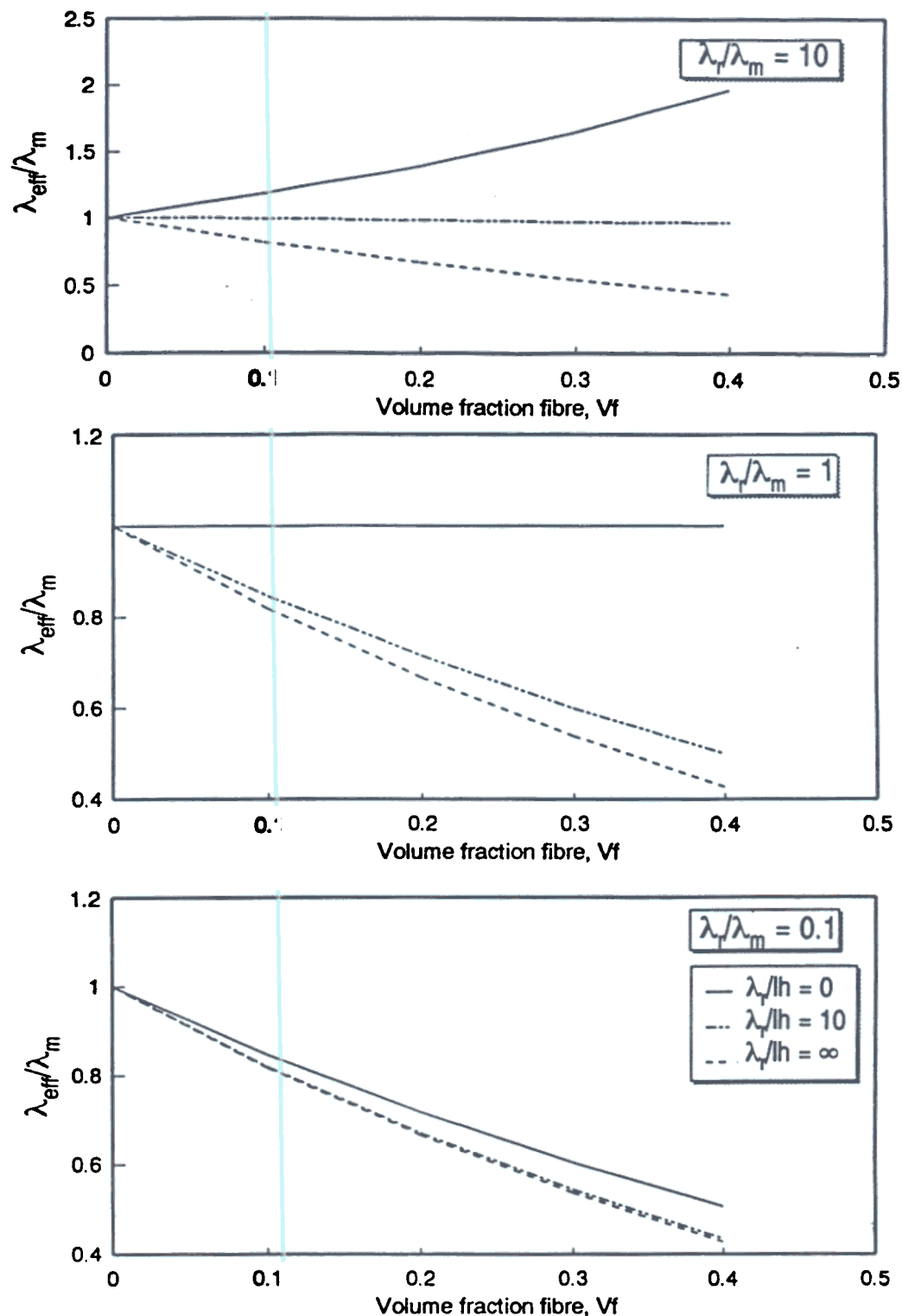


Figure 4 Using the Hasselman and Johnson (1987) equations for transverse thermal conductivity, the effect of fibre volume fraction on the transverse thermal conductivity is shown for various ratios of λ_r/λ_m and for different interfacial thermal conductances h expressed as the non-dimensional parameter λ_r/lh . When λ_r is small compared with λ_m changes to the interface would produce little detectable change in conductivity, but the reverse is true for λ_r much greater than λ_m .