the same plane, that of the crack front.

This is not suggested as alternative to the description of an isothermal/adiabatic transition in fracture behaviour [3], but as a corollary. One can consider the mechanisms in [3] as happening at the molecular level and that in [2] as a phenomenon on the microscopic level, or they can equally well be regarded as cause and effect of the low speed fracture transition in PMMA. This explanation of the stable/unstable fracture transition appears to be consistent with the data in [1] especially when one compares the appearances of the fracture surfaces obtained in these investigations [2, 4, 5], which are strikingly similar.

References

1. A. G. ATKINS, C. S. LEE and R. M. CADDELL, *J. Mater. Sci* **10** (1975) 1381.
2. A. K. GREEN and P. L. PRATT, *Eng. Fract. Mech.* **6** (1974) 71.
3. J. G. WILLIAMS, *Int. J. Fracture Mech.* **8** (1972) 393.
4. A. G. ATKINS, C. S. LEE and R. M. CADDELL, *J. Mater. Sci* **10** (1975) 1394.
5. A. K. GREEN, Ph.D. Thesis, London University (1971).

A. K. GREEN*
*Metallurgy and Materials Science Department,
Imperial College, London, UK*

* Present address: Fulmer Research Institute Ltd, Stoke Poges, Slough, Bucks, UK.

Some studies on the thermal solid state stability of zircon

It is known that the mineral zircon ($ZrSiO_4$) can thermally dissociate to form zirconia (ZrO_2) and either an amorphous form of silica (SiO_2) or a highly siliceous liquid depending on the temperature. However, there is no general agreement as to the temperature at which solid state dissociation begins.

Using X-ray diffraction, Curtis and Sowman [1] carried out a series of investigations on zircon samples of high purity ($\pm$ 99%), including dissociation kinetics, reassociation of dissociated zircon, synthesis of zircon from zirconia and various allotropic forms of silica, and on some phase relations in the system $ZrO_2–SiO_2$. From their experimental conclusions they drew the equilibbrium phase diagram of $ZrO_2–SiO_2$ system presented in Fig. 1. For Curtis and Sowman the domain of the solid state dissociation of zircon is contained between $\sim$ 1540 and $\sim$ 1677° C, 1540° C appearing to be the highest temperature at which zirconia and silica combine to yield zircon and the
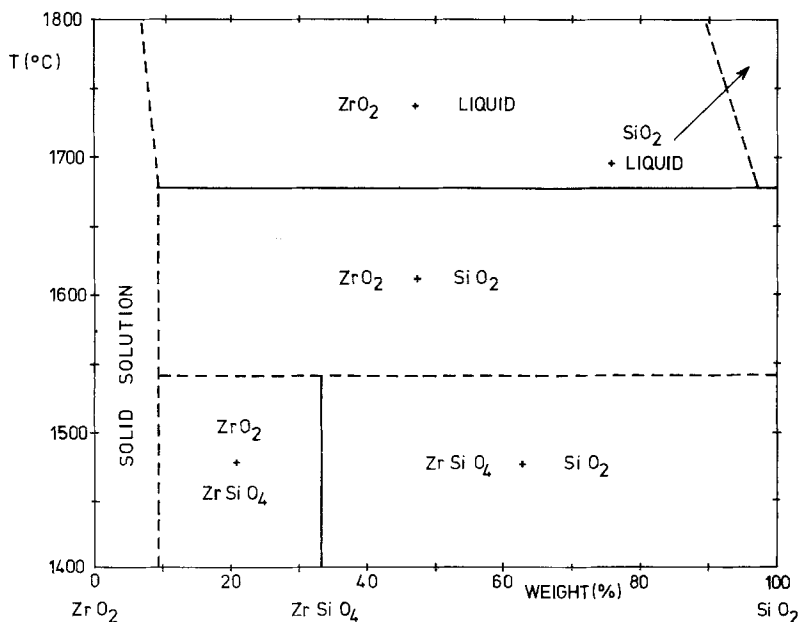

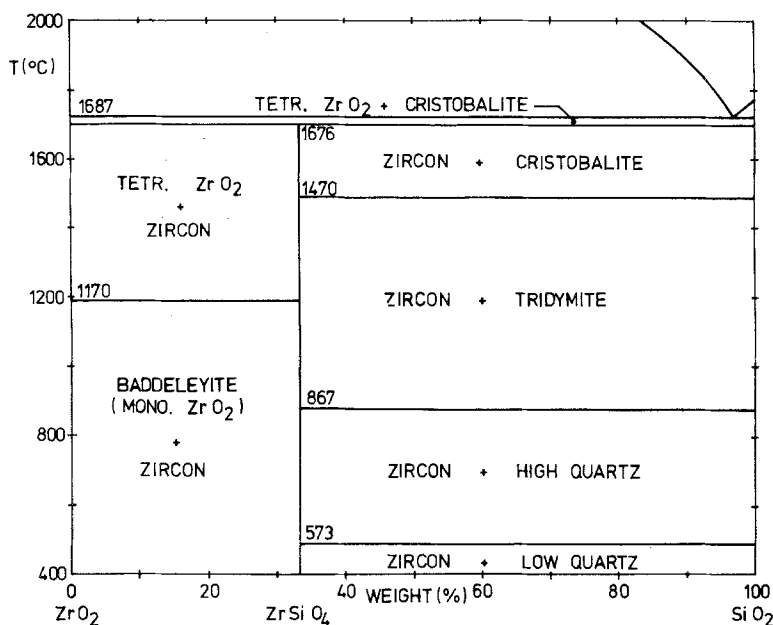*Figure 1* Equilibrium phase diagram of the $ZrO_2–SiO_2$ system proposed by Curtis and Sowman [1].

Figure 2 Equilibrium phase diagram of the ZrO_2–SiO_2 system proposed by Butterman and Foster [2].

lowest temperature at which zircon dissociates to yield the oxides, and $1677°$ C is considered to be the temperature of the eutectic composition which contains ~ 3 wt % ZrO_2.

On the other hand, as a result of X-ray diffraction investigations on the dissociation of purified natural zircon samples and on the synthesis of zircon from the corresponding oxides, Butterman and Foster [2] proposed the equilibrium phase diagram of the system ZrO_2–SiO_2 presented in Fig. 2, which shows that solid state dissociation of zircon exists in a relatively small temperature range (from $1676 \pm 7°$ C to $1687 \pm 4°$ C). Fig. 2 includes the well known inversions in silica and zirconia (monoclinic to tetragonal, tetragonal to cubic) as well as data on the liquid states and does not consider any noticeable solid solubility of silica in zirconia.

By comparing Fig. 1 and 2, it appears that there is disagreement ($\sim 130°$ C) on the lower temperature from which solid dissociation proceeds and approximate agreement on the temperature and the location of the eutectic. It is known that impurities may have a marked influence upon the temperature of dissociation and the synthesis of zircon, but as Curtis and Sowman [1] and Butterman and Foster [2] used zircon, zirconia and silica samples of the highest available purity,

it is unlikely that impurities were responsible for the $130°$ C difference found in the lower limit of solid state dissociation.

In order to clarify this controversy, some investigations on the effect of temperature on dissociation of pure zircon samples have been carried out. The present letter reports the results obtained.

The material used throughout this work was Australian zircon (commercial name Portazir) of high purity (99.13%). The most important impurity proportions estimated by chemical analysis were: Al_2O_3, 0.32 wt %; TiO_2, 0.25 wt %; Fe_2O_3, 0.15 wt %. The grain size distribution is given in Table I.

The tested samples were pressed into bars 3 cm long by 7 cm^2 at 1000 kg cm^{-2} and fired in a graphite furnace. A standard firing programme was followed: $300°$ C h^{-1} temperature rise from room temperature to the desired temperature, 8 h at

TABLE I Typical screen analysis of zircon

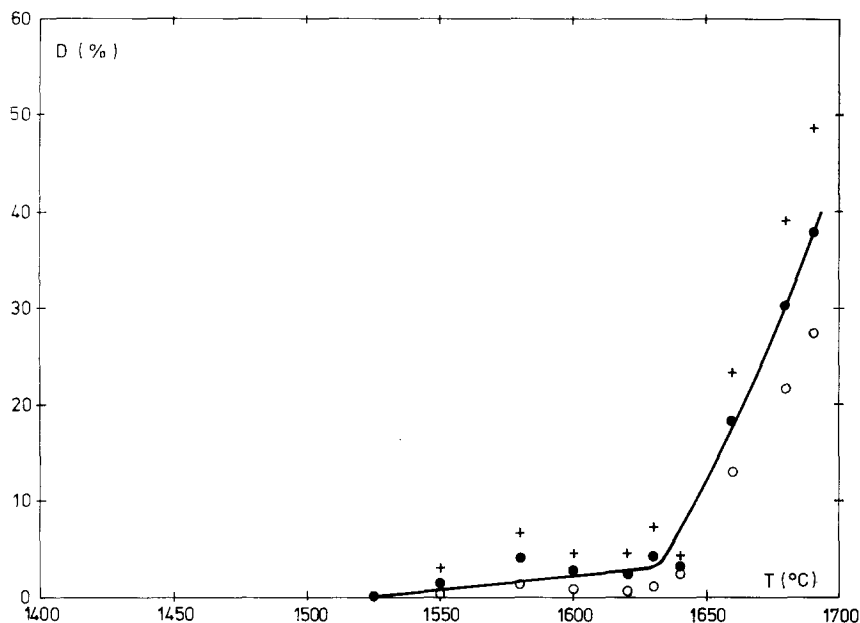| Diameter (μm)	wt %	Diameter (μm)	wt %
>53	0	12–20	18
37–53	2	7–12	19
32–37	14	2– 7	24.5
26–32	6	<2	8.5
20–26	8		

Figure 3 Solid state dissociation observed in Zircon samples fired for 8 h at various temperatures: $+ D_{\text{X-ray}}$ (free zirconia); $\circ D_{\text{Chem}}$. (free silica); $\bullet D$ obtained by average $D_{\text{X-ray}}$ and D_{Chem}.

peak temperature and cooling with the furnace (where the temperature dropped to about 400° C in $\frac{1}{2}$ h and reached room temperature after 24 h). In order to determine the first temperature of dissociation as a function of temperature, the zircon samples were fired for 8 h at 1400, 1450, 1500, 1525, 1550, 1580 1600, 1620, 1630, 1640, 1660, 1680 and 1690° C. After firing, the zircon bars were ground (less than 63 μm) and divided into three portions: one was examined by X-ray diffraction, another was chemically analysed, and third was used for density measurements.

(1) X-ray diffraction measurements. In all cases the degree of dissociation was indicated by the amount (molar percentage) of free zirconia in the fired samples. Room temperature X-ray analyses were obtained with a PW1130 Phillips X-ray diffractometer. A quantitative estimation of zirconia was made by comparing the relative intensities of the strongest diffraction lines of monoclinic zirconia and tetragonal zircon, respectively the (1 1 1) and (2 0 0) lines. A calibration curve was obtained using specimens containing zirconia and zircon in varying percentages. These various standard samples were prepared by mixing zircon (diameter 5 to 20 μm) and ZrO_2 (diameter 7 to 20 μm) for 18 h.

It has been shown that by decreasing the amount of ZrO_2 in the standard mixtures zirconia/zircon,

TABLE II Degrees of dissociation determined using X-ray diffraction and chemical analysis, of zircon samples fired for 8 h at various temperatures

$T(^\circ C)$	$D_{\text{X-ray}}(\%)$	$D_{\text{chem}}.(\%)$	$\bar{D}(\%)$
1400	Undetected	Undected	—
1400*	Undetected	Undetected	—
1450	Undetected	Undetected	—
1500	Undetected	Undetected	—
1525	Undetected	Undetected	—
1550	2.9	Doubtful (0, 2)	1.5
1580	6.5	1.5	4.0
1600	4.4	1.0	2.7
1620	4.4	0.6	2.5
1630	7.2	1.2	4.2
1640	4.4	2.6	3.5
1660	23.4	12.9	18.1
1680	39.0	21.6	30.3
1690	48.5	27.5	38.0

$D_{\text{X-ray}}$ = degree of dissociation determined using X-ray diffraction (molar percentage of free zirconia after firing)

D_{chem} = degree of dissociation determined by chemical analysis (molar percentage of free silica after firing)

$\bar{D}$ = $(D_{\text{X-ray}} + D_{\text{chem}}.)/2$
* = this sample was held for 5 days at 1400° C in Leco furnace.

monoclinic zirconia is detectable down to 2 wt %
using X-ray diffraction. Moreover, as in [1], a
tentative estimation of the accuracy of the degree
of dissociation determined by X-ray diffraction as
±10%. The degrees of dissociation in zircon samples
fired for 8 h as a function of temperature are listed
in Table II and represented in Fig. 3.

(2) *Chemical analysis.* Free silica in the fired
samples was quantitatively analysed by the standard
procedure of attack with HF. The degree of dis-
sociation determined by chemical analysis as a
function of temperature are listed in Table II and
represented in Fig.3.

It must be noted that the process of firing in a
graphite furnace introduces some impurities and,
moreover, that zircon contains some natural
impurities which are attacked and dissolved by the
chemical process used. On the basis of several
checks we estimate that processing natural zircon
in a graphite furnace introduces ±2.5% impurities.
As a loss in weight of 2.7% was found in the
sample fired at 1550° C, we feel it is doubtful that
free silica is present.

(3) *Density measurements.* In order to check
the above results a complete set of density
measurements was performed using a picnometer.

TABLE III Density measurements—comparison of ob-
served data ($d_{obs.}$) with calculated values ($d_{calc.}$)

$T(°C)$	$d_{obs.}(g\,cm^{-3})$	$D(\%)$	$d_{calc.}(g\,cm^{-3})$
1400	4.65	0	4.63
1400*	4.65	0	4.63
1500	4.63	0	4.63
1525	4.63	0	4.63
1550	4.63	1.5	4.62
1600	4.65	2.7	4.62
1620	4.63	2.5	4.62
1630	4.62	4.2	4.57
1660	4.44	18.1	4.40
1680	4.30	30.3	4.25
1690	4.20	38.0	4.17

The results are presented in Table III and in Fig. 4.
Moreover theoretical densities have been calcula-
ted using an average degree of dissociation, $\bar{D}$,
obtained by averaging D_{X-ray} and $D_{chem.}$ (see
Table II), and considering the densities of zirconia,
silica and zircon to be 5.68, 2.05 and 4.63 respec-
tively. The calculated values are in good agreement
with the observed experimental densities.

In the view of the X-ray diffraction experi-
ments and the chemical analysis, which are in
excellent agreement with density measurements,
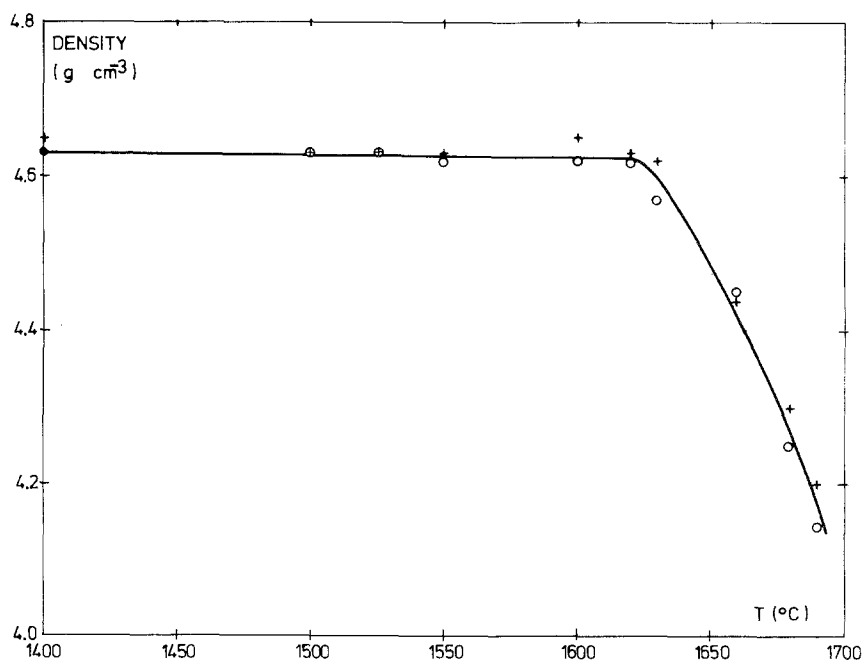it can be stated that solid state dissociation of

Figure 4 Observed and calculated densities of zircon samples fired for 8 h at various temperatures: + experimental data;
○ calculated densities.

581

zircon begins between 1525 and 1550° C, the degree of dissociation remaining small and nearly constant up to ~1650° C, after which it increases rapidly. The results obtained are in excellent agreement with those presented by Curtis and Sowman [1] and, therefore, as far as our studies are concerned, the phase diagram depicted in Fig. 1 appears more reliable that that of Fig. 2.

It must be pointed out that natual zircon constitutes the basis of many refractory materials and a knowledge of the parameters of solid state dissociation of zircon is of importance especially in order to avoid the presence of free silica, which lessens the chemical and mechanical properties of such materials.

References
1. C. E. CURTIS and H. G. SOWMAN, *J. Amer. Ceram. Soc.* **36** (1953) 190
2. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Mineral.* **52** (1967) 880.

M. R. ANSEAU
J. P. BILOQUE
P. FIERENS

Service de Science des Materiaux,
Universite de l'Etat a Mons
Institut National Interuniversitaire, des Silicates,
Sols et Materiaux (INISMa),
7000–Mons, Belgium

## Poisson contraction in aligned fibre composites showing pull-out

When an aligned fibre composite is stretched parallel to the fibres tractions arise across the interface due to the difference in Poisson's ratio between fibre and matrix. This Poisson contraction is usually simple to deal with in the aligned case, because fibres and matrix are subject to the same longitudinal strain. However, in a number of experiments, e.g. pull-out of single fibres and other methods designed to measure the interfacial shear strength, the longitudinal strains in the two components are not the same. In such cases, somewhat different results may be obtained depending upon whether a single fibre or an array of fibres is considered. This is of particular importance in considering interfacial tractions in composites undergoing multiple fracture. In this note we wish to point out why this is so, and to state succinctly some of the consequences.

Consider first a single continuous fibre with Poisson's ratio ν_f embedded in matrix with Poisson's ratio ν_m (Fig. 1), and suppose the whole composite is stretched by an axial strain e. When both fibre and matrix are isotropic, the elastic problem is one of circular symmetry, and is easily solved exactly [1, 2]. The interfacial traction is a normal stress p given by

$$p = \frac{2e\,(\nu_m - \nu_f)\,V_m}{\left[\dfrac{V_m}{k_f} + \dfrac{V_f}{k_m} + \dfrac{1}{G_m}\right]} \quad (1)$$

where k is the plane strain bulk modulus and G
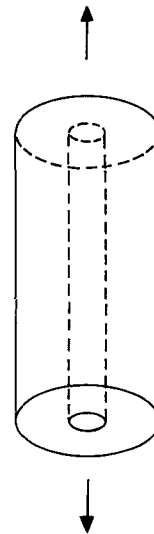
Figure 1 Single fibre imbedded in a matrix.