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Mechanical Properties of Dispersions of Thoria in Beryllia

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The behaviour of the two-phase ceramic system BeO-ThO_2 as a function of thoria (ThO_2) particle size and concentration was studied by measuring changes in strength and Young's modulus. Modulus of rupture measurements were made by the four-point bending of cylindrical specimens, and Young's modulus was calculated from the deflection of rectangular beams. Examination of matching fracture faces showed that cracks passed through thoria particles, indicating they were bonded to the matrix. At 1.6 vol % thoria, the strength of a dispersion depended on the thoria particle size; $\sim$5 μm particles caused little change from 33000 lb/in.^{2} (23.1 kg/mm^2) for pure beryllia (BeO), while with $\sim$110 μm particles the strength was 20100 lb/in.^{2} (14.1 kg/mm^2). The strength of 1.6 vol % $\sim$200 μm dispersions increased with test temperature in the range 20 to 400° C, indicating the presence of internal tensile stresses, caused by the differing coefficients of thermal expansion of beryllia and thoria. Increasing the concentration of thoria caused Young's modulus and strength to decrease; the observed values for Young's modulus agreed closely with those predicted for BeO-ThO_2 dispersions using Hashin and Shtrikman's method. It is concluded that the strength of BeO-ThO_2 dispersions is controlled by the strength of the weak thoria particles unless the particle size is restricted to less than 5 μm.

1. Introduction

The properties of multi-phase brittle solids have been the subject of several previous investigations. Hasselman and Fulrath [1] observed the effect of alumina on Young's modulus of glass. Binns [2], working on alumina and zirconia in glass, and Nason [3], working on tungsten and nickel in glass, demonstrated the presence of internal stresses arising from differences in the coefficients of thermal expansion of the dispersed phases and the glass matrix. The stress system associated with a single, isolated, spherical inclusion was analysed by Selsing [4], who showed that the magnitude of the internal stress was related to the elastic properties of the phases, and to the difference between the coefficients of thermal expansion. Paul [5], Hashin [6], and Hashin and Shtrikman [7] developed models from which the elastic properties of multi-phase systems could be derived if the properties of the components were known.

The present work is concerned with the behaviour of a two-phase system, BeO-ThO_2, in which both phases are crystalline, and in which the beryllia matrix is stronger than the dispersed thoria phase; the effects on the modulus of rupture and Young's modulus of thoria particle size and concentration have been studied over the temperature range 20 to 1000° C. One application of the results lies in the design of dispersion fuel elements in which (UTh)O_2 particles are dispersed in a beryllia matrix [8].

2. Specimens and Their Structures

The thoria particles were prepared by calcination of thorium oxide for 12 h at 900° C in air. The product was isostatically pressed at 20 ton/in.^{2} (32.6 kg/mm^2), crushed, sieved to separate sizes in the range 33 to 600 μm, and finally sintered at 1700° C for 3 h in hydrogen. For sizes below 33 μm, the material was pressed, sintered, crushed, and Cyclosized. The particles were dispersed in an alcohol slurry with UOX beryllia, in the form of as-received powder, −200 mesh. After drying, the dispersion was isostatically pressed at 20 ton/in.^{2}, and sintered at 1500° C for 1½ h in nitrogen.

Dispersions were prepared containing 1.6, 3.5, 7.0, 10.0, 15.0, and 20.0 vol % of ~200 μm diameter particles of 95% dense thoria. In addition, specimens containing 1.6 vol % were prepared with thoria particle sizes of ~5, ~10, ~15, 33 to 53, 53 to 63, 104 to 124, 300 to 350, and 500 to 599 μm.

The structures of the dispersions showed the following features:

(a) The thoria particles were rounded but irregular in shape, and contained about 5% of finely distributed porosity (fig. 1a). Occasional particles were cracked, more noticeably so at the higher concentrations.

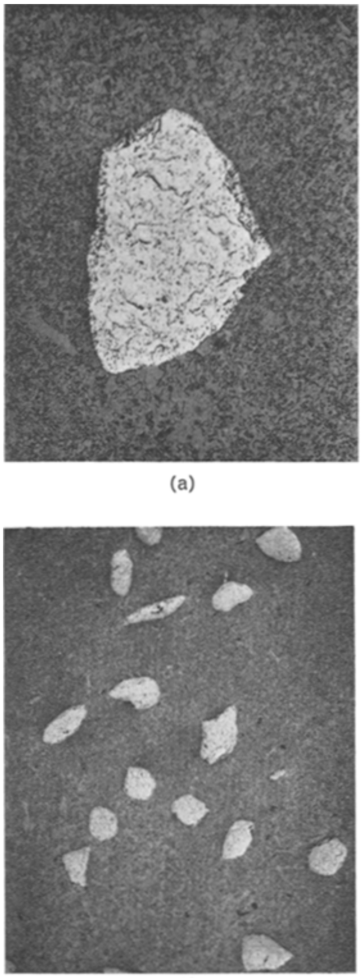
(b) The grain size of the beryllia matrix was generally uniform and less than 5 μm. Occasional areas of coarser grains (10 to 15 μm) were observed adjacent to some thoria particles.

(c) The total porosity of the dispersions increased from 4 to 15% as the concentration of thoria increased from 1.6 to 20.0 vol %.

(d) The uniformity of distribution of the particles varied with concentration. At 1.6 vol %, the particles were generally evenly dispersed; at 7.0 vol %, the particles were less evenly dispersed and they occasionally touched (fig. 1b); whilst at 20 vol %, clustering of the particles was pronounced.

3. Mechanical Properties

The specimens used for modulus of rupture tests were 1.0 in. long (1.0 in. = 25.4 mm) and were centreless ground to 0.160 in. diameter. They were tested in air in four-point bending with a gauge length of 0.313 in. and a span of 0.75 in., at a crosshead speed of 0.03 in./min. Specimens for Young's modulus determinations were surface ground to 3.50 × 0.40 × 0.125 in. They were deflected in four-point bending using a gauge length of 1.50 in. and a span of 3.00 in., and the modulus was calculated using elastic theory from the load-deflection data obtained. Before testing, all specimens were heat treated for 1 h at 1000° C in air, to heal surface cracks in the beryllia produced by the machining operations [9].


(a)

(b)

Figure 1 (a) Thoria particle (×100). (b) 7.0 vol % dispersion of 200 μm particles of thoria in beryllia (×25).

The modulus of rupture of thoria itself, fabricated by the route described above, was measured, and the results are given in table I. The properties of pure beryllia, similar to that

TABLE I Modulus of rupture versus temperature for pure thoria (1 lb/in.^{2} = 7 × 10^{-4} kg/mm^2).

Temperature (° C)	No. tested	Modulus of rupture (lb/in.^{2})	Standard deviation (lb/in^2.)
20	5	11300	2000
400	10	11250	1170
800	5	11350	1075
1000	10	8950	830

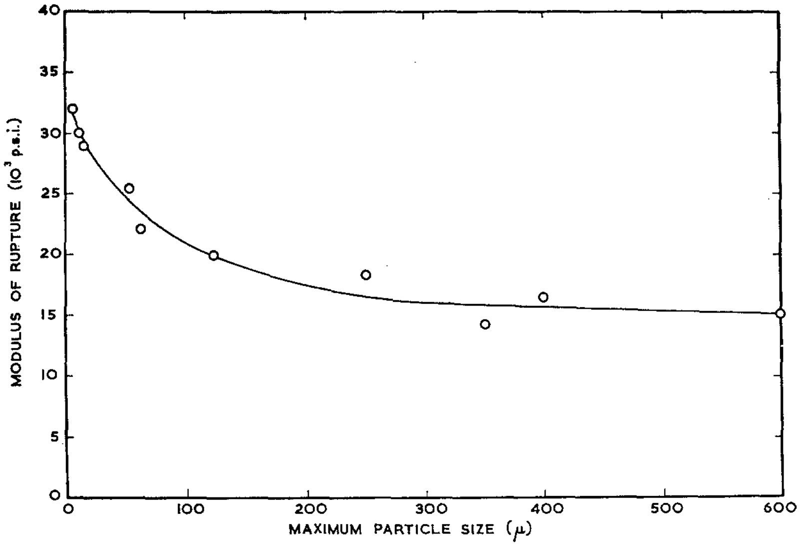


Figure 2 Modulus of rupture versus maximum particle size for dispersions of 1.6 vol % thoria in beryllia. (In the illustrations, p.s.i. is used for lb/in^2. (1 lb/in.^{2} = 7 × 10^{-4} kg/mm^2), and v/o for vol %.)

used in the dispersions, were measured previously by Veevers and Rotsey [10]. The results obtained on the dispersions of thoria in beryllia are given below.

3.1. Modulus of Rupture versus Thoria Particle Size

The results are given in table II, and shown in fig. 2. The strength of the dispersions decreased as the particle size of the thoria increased.

TABLE II Modulus of rupture versus thoria particle size (1 lb/in.^{2} = 7 × 10^{-4} kg/mm)^2.

Thoria particle size (μm)	Porosity (%)	No. tested	Modulus of rupture (lb/in.^{2})	Standard deviation (lb/in.^{2})
5	3.0	5	32100	1420
10	3.0	5	30100	1100
15	4.0	5	29100	4500
33 to 53	2 to 7.0	5	25500	2190
53 to 63	3.0	5	22300	1850
104 to 124	3 to 4.5	5	20100	1245
210 to 250	3 to 5	5	18400	1870
300 to 350	3 to 7	5	14300	3520
350 to 400	2 to 3	5	16600	2540
500 to 600	2 to 5	5	15200	2470

3.2. Modulus of Rupture versus Temperature

Twenty specimens of the 1.6 vol % dispersion containing 210 to 250 μm particles of thoria were tested at each temperature. The results are given in table III and shown in fig. 3, together with the results for pure beryllia and pure thoria.

TABLE III Modulus of rupture versus temperature for 1.6 vol %, 200 μm particles of thoria in beryllia (1 lb/in.^{2} = 7 × 10^{-4} kg/mm^2).

Temperature (° C)	No. tested	Modulus of rupture (lb/in.^{2})	Standard deviation (lb/in.^{2})
20	20	18050	1340
200	20	21050	1560
400	20	22100	2840
600	20	22000	3250
800	20	21250	2320
1000	20	21000	2810

3.3. Modulus of Rupture versus Thoria Concentration

Dispersions containing 210 to 250 μm particles of thoria in concentrations of 1.6, 3.5, 7.0, 10.0, 15.0, and 20.0 vol % were used. The porosity varied, increasing from 3% at 3.5 vol % to 9% at 20 vol % thoria. The results are given in table IV and shown in fig. 4. The strength decreased linearly with increasing thoria concentration.

3.4. Young's Modulus versus Temperature and Thoria Concentration

The porosity of the specimens varied from 4% at 1.6 vol % thoria to 15% at 20.0 vol % thoria. The results of all the tests are given in table V,

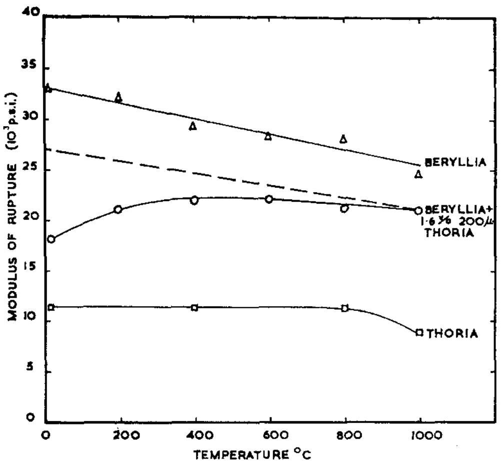


Figure 3 Modulus of rupture versus temperature for beryllia, thoria, and beryllia containing 1.6 vol % 200 μm thoria particles.

TABLE IV Modulus of rupture versus concentration of 200 μm particles of thoria in beryllia (1 lb/in.² = 7 × 10⁻⁴ kg/mm²).

Concentration (vol %)	Porosity (%)	No. tested	Modulus of rupture (lb/in.²)	Standard deviation (lb/in.²)
1.6	4	5	17950	1180
3.5	3	5	17100	1850
7.0	5	5	13550	690
10.0	7	5	12950	1450
15.0	7	5	9000	1120
20.0	9	5	6950	620

and those at 20 and 1000° C are plotted in fig. 5. The variation in porosity caused an apparent anomaly in the data, the 10 vol % having a higher modulus than the 7 vol % dispersion, but generally the modulus decreased as the concentration of thoria increased.

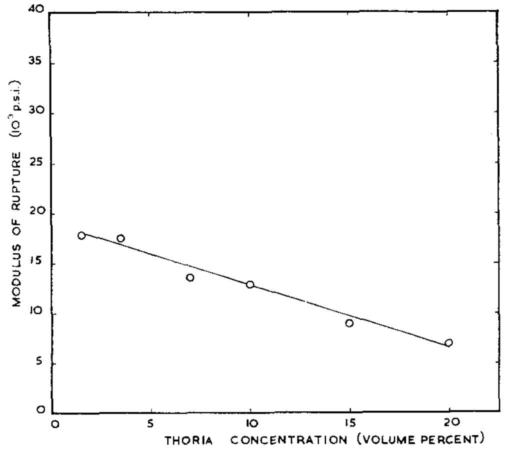


Figure 4 Modulus of rupture versus concentration of 200 μm particles of thoria in beryllia.

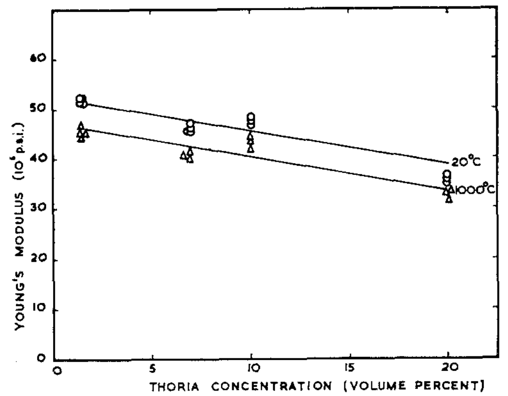


Figure 5 Young's modulus versus thoria concentration.

4. Discussion

The coefficients of expansion of beryllia and thoria over the range 20 to 1000° C have been measured by Turner and Smith [11] as 9.26 × 10^{-6}/°C and 9.75 × 10^{-6}/°C respectively. After a dispersion has been sintered at 1500° C and is cooled, strains resulting from differing coefficients of thermal expansion will initially be relaxed because the beryllia matrix is plastic and creeps readily above 1000° C [12]. As cooling proceeds below 1000° C, the beryllia matrix becomes rigid and cannot creep to match the strain in the shrinking thoria particles. If the thoria particles are strongly bonded to the matrix, tensile stresses will be generated in them; on the other hand, if the bond is weak, the thoria particles will tear away from the matrix and the beryllia will behave as though it contained holes.

Examination of matching fracture faces of dispersions containing thoria particles large enough to identify at relatively low magnifications showed that the fracture had passed through each thoria particle, leaving a fragment embedded in each face. It was concluded that the particles were bonded to the matrix, for, if they were not, the crack would have circumvented them. This observation of bonding between the particles and the matrix was confirmed by measurement of the strength and elastic behaviour of the dispersions as discussed below.

4.1. Effect of Thoria Particle Size

At a constant thoria concentration of 1.6 vol %,

TABLE V Young's modulus versus temperature for various concentrations of 200 μm particles of thoria in beryllia (1 lb/in.^{2} = 7 × 10^{-4} kg/mm^2).

Concentration (vol %)	Porosity (%)	Young's modulus (10^6 lb/in.^{2}) 20° C	200° C	400° C	600° C	700° C	800° C	900° C	1000° C
1.6	4.0	51.8	50.9	51.5	50.8	49.8	49.7	49.0	47.7
	4.5	52.1	51.7	51.7	51.0	50.5	48.7	48.2	46.3
	4.0	52.2	51.8	52.8	51.3	51.7	49.8	48.7	45.6
	4.0	51.7	51.0	50.3	50.3	49.5	48.8	48.2	45.8
7.0	9.2	46.1	46.3	46.5	45.1	44.2	43.2	43.5	40.8
	9.2	45.9	46.1	46.1	45.1	45.0	44.5	43.0	39.3
	8.0	47.5	47.5	48.2	47.5	47.0	45.7	44.7	41.8
10.0	4.0	48.5	47.5	47.7	47.3	47.4	46.3	45.6	45.0
	4.5	47.9	47.3	47.3	47.0	46.6	45.6	44.7	44.2
	4.5	47.3	47.0	47.2	47.2	47.2	45.7	44.5	42.7
20.0	12.4	36.5	36.5	36.2	35.4	34.9	34.7	34.2	32.9
	16.0	35.3	35.6	35.7	35.2	34.4	33.3	33.3	31.6
	15.0	35.8	35.7	35.8	35.8	35.0	34.9	34.1	33.7

the modulus of rupture was little affected by thoria particles of ~5 μm. Increasing the size, however, caused an initial rapid decrease in strength, then a more gradual decrease in the range of 100 to 600 μm particle size (fig. 2). The Young's modulus and bend strength of thoria are both less than those for beryllia, and the strain to fracture is smaller. Consequently, fracture of a dispersion of thoria in beryllia initiates in the thoria particles, and is controlled by the properties of the particles. The stress at which this occurs will be higher than that needed to fracture pure thoria, because the strain is transmitted through the matrix which has a higher Young's modulus. Once the particle size exceeds that of a Griffith crack (in this beryllia about 4 μm at a free surface taking the surface energy to be 10^3dyne/cm^2), a low strength independent of particle size would be expected. A possible explanation of the observed behaviour is as follows.

Weibull [13] has shown that the strength of brittle solids is a function of size, i.e.

$$\frac{\sigma_2}{\sigma_1} = \left(\frac{V_1}{V_2}\right)^{\frac{1}{m}}$$

where σ_1 is the strength of material of volume V_1; σ_2 that at V_2; and m, a constant.

The thoria particles have very different volumes, for example, particles of diameter 5, 50, and 500 μm have volumes in the ratio $1:10^3:10^6$, and the strength should therefore vary. The strengths of dispersions shown on the curve in fig. 2 may be taken to be directly proportional to the strengths of the thoria particles, since fracture initiates in the particles, and, knowing the ratios of the strengths and volumes of various sizes of thoria particles, the Weibull coefficient, m, can be evaluated. The data was fitted to the Weibull relation (fig. 6) giving m = 13.9, a value typical of high-grade ceramics [14].

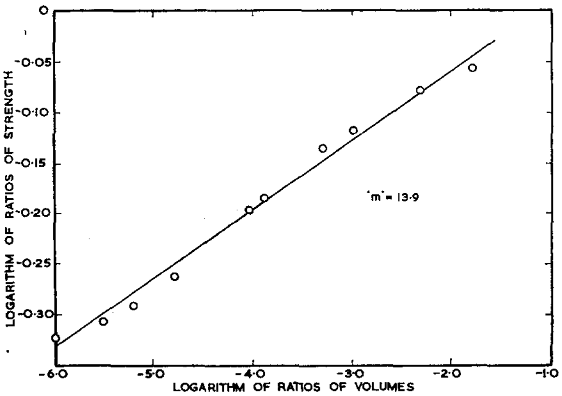


Figure 6 Derivation of Weibull constant from fig. 2.

4.2. Effect of Temperature

An increase in strength was observed as the test temperature of the dispersions was raised above 20° C (fig. 3). The results at 200 and 400° C were shown to be statistically higher than those at 20° C to the 0.1% significance level. Neither beryllia nor thoria increased in strength on heating, and the probable explanation for the behaviour of the dispersions is that internal tensile stresses in the thoria particles, arising from the differing coefficients of expansion of beryllia and thoria, were relieved as the test temperature was increased. The dashed line in fig. 3 indicates the behaviour which may be expected from the dispersions if internal stresses were absent. Thus, although internal stresses are generated throughout the cooling range, their effect does not become obvious until the temperature falls to about 400° C.

Although the coefficients of thermal expansion of thoria and beryllia differ by only $0.5 \times 10^{-6}/°$ C, this can result in very large stresses in the temperature range 20 to 1000° C. The value of the internal stresses after cooling to 20° C may be calculated, from Selsing's equations [4] and the data used in section 4.3, to be about 21000 lb/in.^{2} (14·7 kg/mm^2) at the surface of the particle. The observed modulus of rupture will not change by this amount, because it is a measure of a bulk property. The local strength, such as measured by indentation tests, which is very much higher than the bulk strength, may actually be reduced by 21000 lb/in.^{2} and this may in turn result in a smaller reduction in the modulus of rupture.

4.3. Effect of Thoria Concentration

The variation of Young's modulus with composition for bonded two-phase systems has been calculated by Hashin and Shtrikman [7], using variational principles for non-homogeneous linear elasticity. Upper and lower bounds are predicted by the equations

$$K_1{}^* = K_1 + \cfrac{v_2}{\cfrac{1}{K_2 - K_1} + \cfrac{3v_1}{3K_1 + 4G_1}}$$

$$K^* = K_2 + \cfrac{v_1}{\cfrac{1}{K_1 - K_2} + \cfrac{3v_2}{3K_2 + 4G_2}}$$

$$G_1{}^* = G_1 + \cfrac{v_2}{\cfrac{1}{G_2 - G_1} + \cfrac{6(K_1 + 2G_1)v_1}{5G_1(3K_1 + 4G_1)}}$$

$$G_2{}^* = G_2 + \cfrac{v_1}{\cfrac{1}{G_1 - G_2} + \cfrac{6(K_2 + 2G_2)v_2}{5G_2(3K_2 + 4G_2)}}$$

$$E = \frac{9K^*\,G^*}{3K^* + G^*} \text{ and } \mu = \frac{E}{2G} - 1$$

where K_1, K_2, K^* are the bulk moduli of phase 1, phase 2, and the dispersion, respectively; G_1, G_2, G^* are the shear moduli of phase 1, phase 2, and the dispersion, respectively; E is the Young's modulus of dispersion; v_1 and v_2 are the fractional concentrations of phase 1 and phase 2 respectively; and μ is Poisson's ratio.

To apply this to the BeO-ThO$_2$ dispersions, knowledge of the elastic properties of both phases is required.

Three specimens of pure beryllia, identical to that used for the matrix of the dispersions, were sintered with the dispersions. The porosity was 2.5% and the Young's modulus was 53×10^6 lb/in.^{2} (1 lb/in.$^2 = 7 \times 10^{-4}$ kg/mm^2). The matrices of the dispersions, however, had porosities varying from 4 to 16%. The variation of Young's modulus with porosity was previously measured for this type of beryllia by Veevers and Rotsey [10], who obtained the relation

$$E = E_0\,(1 - 1.47\,P)$$

where E is Young's modulus at porosity P, in lb/in.^{2}; E_0, that at zero porosity; and P, the fractional porosity by volume. The values of Young's modulus for the various matrices were therefore estimated from the relation

$$E = 55 \times 10^6\,(1 - 1.47\,P) \text{ lb/in.}^2$$

Young's modulus for the thoria particles was taken to be 35.0×10^6 lb/in.^{2} [15], and Poisson's ratio was taken to be 0.27 for beryllia [16] and 0.30 for thoria. The upper and lower bounds of Young's modulus for the dispersions were calculated but, because the elastic moduli of the two phases only differed by a factor of 1.5, the upper and lower bounds were almost coincident, the variations being at most 0.1×10^6 lb/in.^{2} The values for the upper bounds are given in table VI.

Comparison with the observed values showed good agreement except for the 20 vol % dispersion, where the particles were so numerous that they were clustered or very close to one another with interparticle voids or areas of low density. In this case, the assumptions made in Hashin and Shtrikman's derivation were probably invalidated.

TABLE VI Comparison between observed and calculated values for Young's modulus at 20° C for dispersions containing 200 μm particles of thoria (1 lb/in.^{2} = 7×10^{-4} kg/mm^2).

Total porosity (%)	Thoria content (%)	Young's modulus (10^6 lb/in.^{2})		
		Calculated value assuming thoria is unbonded	Calculated value assuming thoria is bonded (Hashin and Shtrikman)	Observed value
4.0	1.6	50.6	51.5	51.8
4.5		50.2	51.2	52.1
4.0		50.6	51.5	52.2
4.0		50.6	51.5	51.7
9.2	7.0	42.2	46.3	46.1
9.2		42.2	46.3	45.9
8.0		43.0	47.6	47.5
4.0	10.0	43.8	49.8	48.5
4.5		43.5	49.6	47.9
4.5		43.5	49.6	47.3
12.4	20.0	28.8	43.1	36.5
16.0		25.9	40.6	35.3
15.0		26.7	41.6	35.8

If the thoria particles were not bonded to the matrix, the total porosity could be computed to be the sum of the volume of natural porosity in the matrix plus the volume of thoria, e.g. a specimen containing 8% porosity and 7 vol % thoria would be regarded as having 15% total porosity. The calculated values of Young's modulus based on this assumption (table VI) show poor agreement with the observed values. The decrease in strength as the thoria concentration increases is due to several factors. In part, it is caused by the increase in porosity of the matrices from 4% at 1.6 vol % thoria to 9% at 20 vol % thoria. A further contribution arises from the "Weibull" effect; as the concentration, and therefore the volume, of thoria increases, so does the probability of the presence of a weaker thoria particle. Finally, the decrease of Young's modulus with increasing thoria concentration will also cause a decrease in fracture strength. The 10 vol % dispersion has a modulus of rupture 28% lower than the 1.6 vol % dispersion. The increase in porosity would account for a decrease of ~7%, the Weibull effect (using $m = 13.9$) contributes a further decrease of 12.5%, and the decrease in Young's modulus would cause a decrease of 4%, which, taken cumulatively, gives a total decrease of ~24%, in fair agreement with the observed value. Such a calculation for the 20 vol % dispersion cannot account for the observed decrease of ~60% compared with the 1.6 vol % dispersion. However, the anomaly may be associated with the microstructures of the 15 and 20 vol % dispersions, which revealed that in these dispersions some thoria particles were cracked, and in places where particles were clustered the matrix frequently contained interparticle voids or areas of low density. The effect of the inferior structures was also evident in the low Young's modulus (see above).

4.4. Application to Dispersion Fuels

The general principle of a dispersion fuel, such as UO_2 in stainless steel, or UAl_2 in aluminium, is that the integrity of the fuel element depends on the inert matrix, and is independent of the fuel phase. BeO-ThO_2 dispersions are converted into fuels for high-temperature reactors by the addition of enriched UO_2 to the thoria particles, giving a solid solution $(UTh)O_2$. This work has shown that the strength of such fuels is likely to depend on the fuel particle, thus violating the principle of design of dispersion fuels. In order that the dispersion properties depend on the matrix, the fuel particles must be reduced in size to about 5 μm. Hilditch *et al.* [17] irradiated $(UTh)O_2$ dispersed in beryllia and found that, after a burn up of 3.5 to 5 at. % of heavy metal atoms at temperatures below 600° C, the strength of the 5 μm dispersion was slightly reduced, whereas that of the 200 μm dispersion was drastically reduced. Thus, the higher, unirradiated strength obtained by the use of 5 μm particles was retained under irradiation. This result was contrary to that expected, since the volume of matrix bombarded by fission fragments was greatest in the 5 μm dispersion, and it was concluded that fission fragment bombardment in some way reduced the effects of fast neutron damage in the matrix.

5. Conclusions

(a) The behaviour of BeO-ThO_2 dispersions indicated that the thoria particles were bonded to the beryllia matrix.

(b) The differing coefficients of thermal expansion of beryllia and thoria gave rise to internal stresses at low temperatures.

(c) Young's modulus of dispersions decreased as thoria concentration increased; the observed values agreed well with those predicted by Hashin and Shtrikman's method for coherent inclusions.

(d) Additions of thoria to beryllia caused a reduction in modulus of rupture, the greater the concentration of thoria, the weaker the dispersion. At a constant concentration of thoria, the strength of the dispersion depended on the thoria particle size, the larger the particle, the weaker the dispersion.

(e) The strength of a two-phase ceramic system in which the dispersed phase has a smaller strain to fracture than the matrix, is controlled by the properties of the dispersed phase, unless the particle size of the dispersed phase is limited to that of a Griffith crack in the matrix. For BeO-ThO_2 dispersions, the maximum permissible size of thoria particles is about 5 μm.

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