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The room temperature fracture strength of sintered UO_2 rings containing deliberately introduced impurities

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A ring test has been used to measure the room temperature fracture strength of sintered UO_2 and of UO_2 deliberately doped with either silica, calcium oxide or iron oxide. The maximum observed flaw size and the minimum measured fracture strength in a group of nominally identical specimens was found to be related for some of the materials tested. It is shown that the additions of silica and calcium oxide do not appear to alter the energy for fracture initiation. Fracture strength measurements obtained using the ring test, where the applied stress is relatively uniform over the specimen cross-section, and the three-point bend test where it is not, fit the same strength/flaw size relationship provided minimum measured strength is associated with maximum flaw size.

1. Introduction

The effect of impurities on the fracture of UO_2 is largely unexplored despite the fact that cracking of the fuel may affect the in-reactor performance of fuel elements. Knudsen *et al.* [1] have reported that additions of 0.25 wt % titania to UO_2 decrease the rupture modulus by about 20% at room temperature but have no effect at 1000° C, whereas 0.75 wt % titania, which produced grain-boundary precipitates, increased the rupture modulus by 20 and 90% at room temperature and 1000° C respectively. Titania is not, however, a major impurity in UO_2; more important are elements such as calcium, magnesium, aluminium, silicon and iron. Magnesium, added as 0.75 wt % magnesia, has been shown to reduce the room temperature fracture strength of ring specimens by about 25% relative to UO_2 [2]. Goodyear *et al.* [3] observed random changes from transgranular to intergranular in the room temperature fracture mode of UO_2 specimens taken from a single batch and attributed these to the presence of silicon as a grain-boundary impurity, while in a recent paper [4], Solomon has also shown that silicon-containing particles produce a marked reduction in the room temperature fracture stress of UO_2 and that alumina has a similar effect. By comparison metallic iron or uranium were found to have no significant effect.

This paper reports the results of an investigation into the effects of deliberate additions of silica, calcium oxide and iron oxide on the room temperature fracture strength. Silicon, calcium and iron are all major impurities in UO_2 and the quantities present in production oxide show considerable batch-to-batch variations. The quantities added were 10 to 15 times those normally present.

2. Experimental

2.1. Apparatus

The apparatus used in the present work is shown in Fig. 1 and is a slightly modified version of that previously described [5]. The cylindrical piston of the earlier apparatus, which is shown in Fig. 1 of [5], has been replaced by a composite piston J and plunger K to reduce sticking. In operation, the apparatus is placed between the platens of an Instron test machine operating in compression.

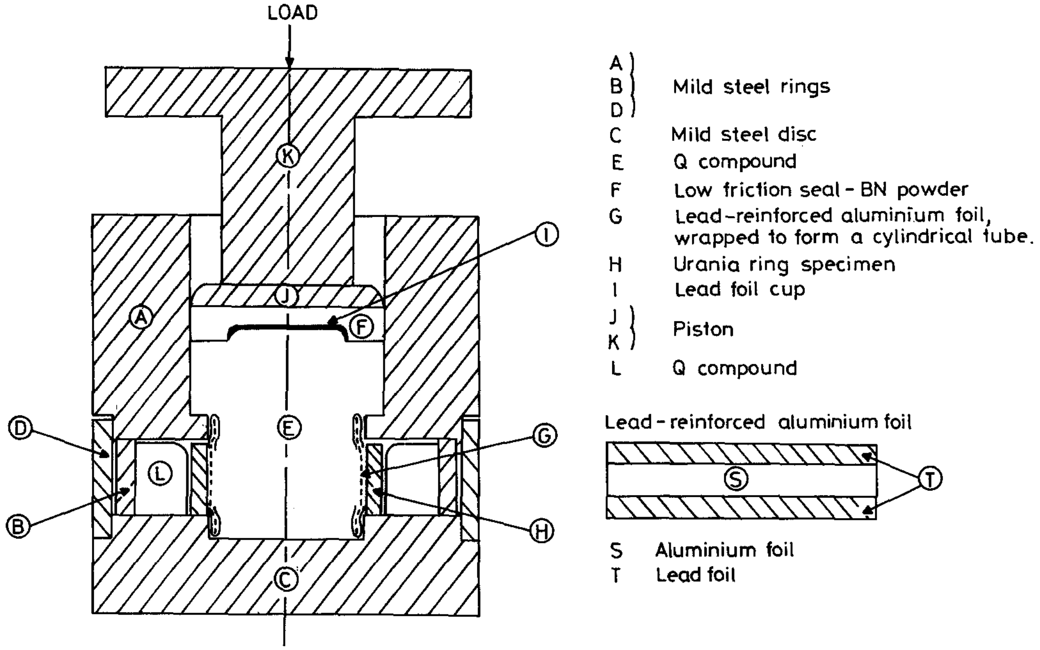

Figure 1 Improved ring test equipment.

The load is transmitted hydraulically through Apiezon "Q"-compound (E in Fig. 1) to the specimen in which it produces a tensile hoop stress.

To identify the fracture surface, it is necessary to prevent shattering occurring by impact with the metal ring B at the instant of fracture. Q-compound is, therefore, placed at L so that it surrounds the test specimen leaving only a small annular gap. With this arrangement, the broken rings consist of a few pieces only. To locate the point of primary fracture, the foil G was designed to split at this point and to facilitate this, the previously used lead foil was replaced by one of aluminium reinforced at its edges with a double thickness of 0.15 mm thick lead.

2.2. Specimen fabrication

Micronized UO_2 powder was blended, where necessary, with the required quantities of silica, calcium oxide or iron oxide by sieving the powders together repeatedly through a 250 μm (60 BSS) sieve and then milling for 2 h with steel balls. After blending with an organic binder the powder was granulated and pressed into thin-walled rings which were debonded by heating in a 1:1 CO_2/H_2 mixture for 1 h at 900° C. The rings were finally sintered in hydrogen at 1650° C. The dimensions of the as-sintered rings were 19.5 mm i.d. 23.6 mm o.d. and 10 mm tall. Details of the various specimen types are given in Table I. The grain sizes quoted are mean unadjusted intercept lengths.

TABLE I Specimen details

Batch no.	Additive	Concentration (at. % cation with respect to U)	Density ($Mg\,m^{-3}$)	Grain size (μm)	Max. flaw size (μm)
1	SiO_2	0.34	10.67	5.8	1670
2	Fe_2O_3	0.30	10.73	7.4	180
3	CaO	0.2*	10.70	8†	570
4	CaO	0.2*	10.70	8†	600
5	CaO	0.33	10.64	7.7	195
6	CaO	0.6*	10.60	8†	170
7	none	–	10.80	10.7	400

* Nominal values – not checked by chemical analysis.
† Estimate from examination of fracture surfaces.

3. Results

3.1. Silica-doped material

The room temperature fracture strength measurements are shown in Table II. The mean strength is 40.8 $MN\,m^{-2}$ and the median fracture strength, based on a Weibull-type of analysis [6] in which the limiting stress, σ_u is assumed to be zero, is 41.2 $MN\,m^{-2}$.

The maximum pore size in these specimens was 300 μm but fissure-like flaws up to 1670 μm long were also found. A characteristic of these fissures is that their extremities narrow down until they appear as cracks so that the material

TABLE II Fracture strength data

Batch no.	Measured fracture strengths (MN m^{-2})								Min. fracture strength (MN m^{-2})	Min. group strength (MN m^{-2})
1	24.3	25.7	27.7	29.7	36.5	37.1	37.1	39.2	24.3	24.3
	39.3	39.3	41.9	41.9	43.2	43.2	43.9	44.6		
	46.6	48.6	48.6	52.7	53.3	54.0				
2	20.3	31.1	35.1	36.5	43.2	51.3	59.4	62.1	20.3	20.3
	62.8	63.5	64.2	66.9	69.6	70.3	70.3	70.9		
	71.6	72.3	73.7	75.0	76.3	77.0	83.1			
3	36.6	38.5	50.0	58.1	60.4	63.7			36.6	36.6
4	4.1	44.7	62.8	69.1	70.2	74.4	77.0		4.1	44.7
5	22.2	23.6	25.6	29.0	35.7	37.7	40.4	41.1	22.2	22.2
	48.5	60.6	62.0	62.7	66.7	68.7	70.1	70.1		
	71.4	72.1	73.4	74.1	78.8	81.5	87.6			
6	17.6	37.6	50.2	53.7	56.7	62.1	65.8		17.6	17.6
	66.2	66.8	70.8							
7	50.9	60.8	65.9	69.0	75.1	79.4	82.8		50.9	50.9

appears to be splitting. They are probably caused by differential shrinkage during sintering rather than by the silica addition *per se* since cylindical pellets, made from the same powder, did not contain them. Similar flaws were also observed in some of the calcium oxide-doped material discussed later. Although the silica was added as a fine powder and its mean particle size is unknown, it is certainly considerably coarser than the silica normally present as an impurity in UO_2 which probably derives from water used in the powder preparation.

Silica can be reduced by hydrogen to form gaseous silicon monoxide, and Smithells [7] has estimated the free energy, ΔG^0, of the reaction

$$2\,SiO_2 \rightleftharpoons 2\,SiO + O_2$$

to be

$$1556 - 0.517\,T\ \text{kJ mol}\ O_2\ (300\ \text{to}\ 1770\,\text{K}) \quad (1)$$

and

$$1623 - 0.554\,T\ \text{kJ/mole}\ O_2\ (1770\ \text{to}\ 2000\,\text{K}). \quad (2)$$

The oxygen potential of the hydrogen used as the sintering atmosphere is typically between -420 and -540 kJ mol^{-1} which would be in equilibrium with a silicon monoxide pressure of between 2 and 105 kN m^{-2} at 1650° C so that, provided the kinetics of reaction are favourable, the monoxide will form at the sintering temperature. However, by the time the temperature has reached 1400° C and most of the porosity has closed, the pressure of SiO will, on the basis of Equation 1, be at most 0.5 kN m^{-2} so that it is unlikely that much loss of silicon will occur. Nonetheless, the quantity of silicon found during analysis of these rings was only about 80% of that expected from the composition of the UO_2/SiO_2 powder.

Silicon was detected with the electron probe microanalyser in many of the large pores, although the extent, if any, of its combination with oxygen could not be assessed. It was not, however, associated with carbon. The electron probe microanayser cannot be used satisfactorily to examine the surfaces of deep cavities but silicon could be detected at the ends of the large fissures referred to earlier, and scanning electron microscopy revealed a second phase with the morphology characteristic of a gaseous deposit, presumably of silicon monoxide.

Having observed silicon in the pores of deliberately doped material, large pores in other materials which had not been deliberately doped with silica were also examined and a silicon-containing second phase, which appeared to have grown from the vapour, was frequently seen. Silicon, therefore, seems generally to be present on pore surfaces, and in view of the very small amount of silicon monoxide needed to fill the porosity at a pressure of 0.1 MN m^{-2}, it is reasonable to assume that this deposition arises by a silica reduction/SiO decomposition mechanism.

In all the specimens which were examined optically at high magnification, numerous submicron bright "inclusions" were observed. It was thought that these might be silicon-bearing material trapped in small pores, and a scanning electron microscope examination of one particular "inclusion" previously seen as a bright reflecting material with the optical microscope revealed that it was, in fact, a pore containing a small quantity of a second phase. An attempt was made to etch out any material that might be present in these "inclusions". The nitric-hydrofluoric acid used as the etchant attacks UO_2 and should also dissolve silicon oxides but produced no reduction in the density of bright "inclusions" suggesting that as the UO_2 surface is dissolved, the new surface, which is exposed, contains a similar density of "inclusions".

3.2. Iron-doped material

Individual measurements of fracture strength are shown in Table II and from these the mean and median strengths are calculated to be 61.9 and 61.2 MN m^{-2}, respectively. The standard deviation from the mean is ± 16.4 MN m^{-2}. The largest flaws in this material were pores with a maximum size of 180 μm. In general the appearance under the microscope was similar to that of undoped UO_2 except that here the pores were smaller and the iron inclusions up to 80 μm diameter were both larger and more numerous than in the pure material where their size was about 1 μm. The inclusions had obviously been molten at the sintering temperature.

Compared to previously tested pure material [5] the scatter of the measured strengths is greatly increased, although the mean fracture strength is not significantly changed. As will be seen later, the minimum strength does not relate to the maximum observed flaw size. The large pores do not appear to be connected in any way with the presence of iron and it is possible that they arose in the same way as the even larger pores observed in the undoped UO_2.

3.3. Calcium oxide-doped material

3.3.1. Concentration 0.33 at. % calcium

This batch of calcium oxide-doped UO_2 was the most extensively tested. Table II shows the results of the fracture strength measurements. From them, the mean and median strengths have been calculated to be 56.7 and 56.6 MN m^{-2} with the standard deviation of the former being ± 20.0 MN m^{-2}.

The addition of calcium oxide had a marked effect on the microstructure of the rings, producing numerous large pores typically between 20 and 50 μm in diameter. The largest pores were up to 195 μm diameter and a few fissure-type flaws, smaller than the largest pores were also observed. Since calcium oxide can form a solid solution with UO_2 and since also the quantity added is relatively small, the magnitude of the effect on the microstructure is, at first sight, surprising. However, during binder removal, the rings are heated in an atmosphere containing carbon dioxide at a partial pressure of 35 to 50 kN m^{-2} and favourable conditions are thus established for the formation of calcium carbonate. During sintering, however, the carbonate will decompose probably before much densification has occurred, with the evolved carbon dioxide able to form cavities in the UO_2, probably a cavity forming for each particle of CaO. Experiments with doped pellets which were sintered for between 0.5 and 120 h at 1650° C showed similar large pores to those found in the ring specimens, the only visible effect of the more extended sintering being the progressive rounding of the porosity, thus showing that the large pores form at an early stage.

Normally, calcium in UO_2 probably enters as impurity in water during powder preparation and hence will be much more finely dispersed than when deliberate additions of powder are made. It would not, therefore, be expected that this normal impurity calcium would have anything like so marked an effect on the UO_2 microstructure.

3.3.2. Concentrations 0.2, 0.4 and 0.6 at. % (nominal)

Since calcium oxide produced numerous large pores, an attempt was made to investigate the effect of flaw density on strength. Specimens were fabricated which contained calcium concentrations of 0.2, 0.4 and 0.6 at % (nominal) with respect to uranium. Details are given in Table I but are more sketchy than for the other materials since less characterization was carried out. In particular, the grain sizes are estimates made by examination of fracture surfaces. Table II shows the results of the fracture strength measurements which were made on these batches of rings. The mean and median fracture strengths are summarized in Table III.

The flaw pattern in these samples was surprising In the batches containing 0.2 and 0.4 at % calcium, large fissure type flaws such as were found in the silica-doped specimens were seen and this

TABLE III Mean and median fracture strengths

Batch no.	Mean fracture strengths ($MN\,m^{-2}$)	Standard deviation ($MN\,m^{-2}$)	Median fracture strength ($MN\,m^{-2}$)
1	40.8	8.5	41.2
2	61.9	16.4	61.2
3	51.2	10.5	51.9
4	66.4	10.7	67.1
5	56.7	20.0	56.6
6	54.7	14.8	54.9
7	69.1	10.3	69.7

prevented the planned study of pore density being carried out. These flaws are thought to be a result of differential shrinkage during sintering, possibly as a consequence of granules of UO_2 not being deformed during compaction to form the green ring. The loosely agglomerated material in such a region is likely to sinter to a different extent and possibly at a different rate from normally compacted UO_2 and any tensile stress developed could then be relieved by formation of a fissure. Fig. 2 shows the way in which the large fissures are frequently associated with low density regions of the ring.

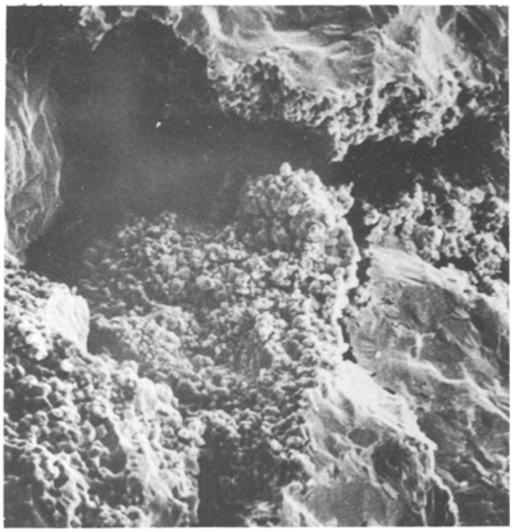

Figure 2 Scanning electron micrograph of fracture surface of calcia-doped specimen showing loosely sintered material thought to be remnants of a granule.

The third batch of rings did not contain these large fissure-like flaws but had, instead, a microstructure resembling that of the first batch of calcium oxide-doped rings. Both the maximum flaw size and the mean fracture strength were similar.

3.4. Undoped UO_2

This material was relatively free from large pores. However, the largest pores were of greater size than any which occurred in the batches of doped material, several being in the range 250 to 400 μm Table I again shows specimen details. The mean fracture strength was 69.1 ± 10.3 $MN\,m^{-2}$ and the median strength 69.7 $MN\,m^{-2}$, the highest of all the batches.

The origin of the largest pores in these specimens, and in those containing the deliberately added impurities, is not known. Non-uniform packing of the granulated powder and binder might be a possible cause.

4. Discussion

A feature of the present work is the large scatter in the measured strengths for each batch of specimens. This highlights the problem of relating strengths to flaw-size data. Normally, mean strengths would be used but this creates the problem of choosing a mean or corresponding flaw size. The ideal solution to the problem, which avoids any discussion of probabilities, would be to determine the size of flaw responsible for fracture in each specimen individually. An attempt to do this was made by examining fracture surfaces with the scanning electron microscope but was unsuccessful for reasons which might be associated with fragmentation occurring at the fracture surface in the region of the failure-inducing flaw.

An alternative, though less satisfactory, approach which appears to work for at least some of the present data, is to assume the minimum strength of a batch to be associated with the flaw of maximum size which is favourably oriented and which is characteristic of that batch of specimens, the most damaging being surface flaws. The behaviour of all other specimens in a batch is then explained by assuming that the largest flaws in these specimens were either smaller, less favourably orientated or positioned.

The terms maximum flaw size and minimum strength require further discussion. The maximum flaw size is taken as the maximum dimension of the largest flaw observed during optical microscopy of a polished section. If the number of large flaws were small, the probability of finding the maximum dimension of the largest flaw in any metallographic section would also be small, but in such a case, the probability of such a flaw being favourably positioned to dominate the failure characteristics of the specimen should also be small. Conversely, if several similar sized large flaws are observed in the sections examined, as occurred with all the batches in the present work, the number in any specimen must be relatively large so that the probability that some specimen in the batch will have a similar-sized flaw favourably orientated should also be high. If a specimen should fail because of an even larger but uncommon flaw, it might be expected that the fracture strength would not be grouped with the other values for the particular batch of specimens. The minimum strength of a batch is, therefore, taken as the lowest of the grouped values of fracture strength and with one exception, the calcium-oxide doped specimens which contained 0.4 at.% Ca, it is the lowest strength observed. The corresponding flaw size is taken as the largest flaw generally observed and in all the batches is, in fact, the largest actually observed.

The strength–flaw size data are plotted in Fig. 3 as maximum and minimum fracture strengths for each specimen batch versus $c^{-1/2}$, where c is the maximum flaw size. It can be seen that the minimum strengths of four batches, those doped with silica, with 0.2 and 0.4 at.% calcium and batch 7 of undoped UO_2 lie close to a straight line drawn through the origin. Now because these specimens have similar densities and hence are expected to have similar values of Young's modulus, the linear relationship implies that these specimens have similar values for the energy of fracture initiation. Thus it would appear that silica and calcia, at the levels employed in these batches, do not affect the fracture energy.

For the remaining batches, flaw sizes about a factor of ten larger than observed would be required to cause their minimum strength values to coincide with the line. Since the majority of the specimens from these batches have strengths below the line, it is surprising that no trace of such large flaws could be found, even though the search for them was especially thorough. An explanation based on the existence of these large flaws would seem, therefore, to be inadequate. Nor is it thought that the results can be explained in terms of changes in surface energy brought about by the presence of impurities. The surface energy would have to be reduced by a factor of ten and, in any case, two of the four calcium oxide-doped batches fall on the line shown in Fig. 3. It is possible, however, that these batches were under significant

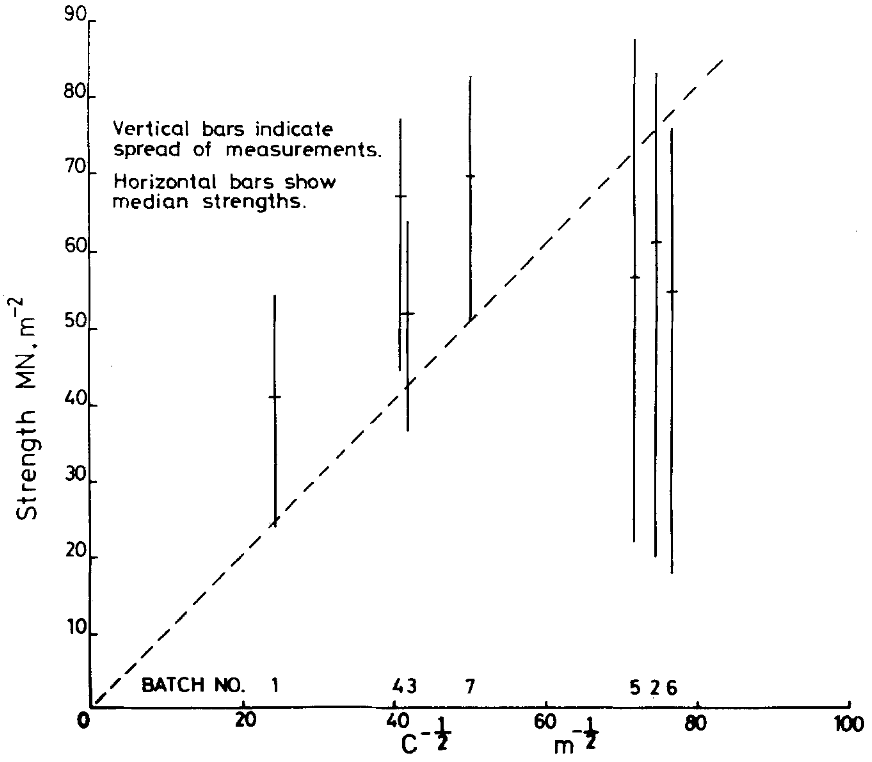

Figure 3 Measured strengths as a function of $c^{-\frac{1}{2}}$.

residual stress after sintering. It is noteworthy that they have the smallest measured maximum flaw sizes in the range 170 to 195 μm compared with 400 to 1670 μm in the other four batches. Three of these latter batches have the large fissure-like flaws which are thought to be caused by differential shrinkage during sintering. It is possible that stresses arising during sintering are reduced by the formation of these fissures. Furthermore, Armstrong and Irvine [9] have shown that UO_2, doped with calcium oxide has a lower creep rate and sinters more slowly than UO_2 so that any tendency to build-up stresses during sintering might be accentuated in this material and, on the evidence of Armstrong and Irvine's work this tendency would be expected to increase with increasing concentration of dopant. It requires the addition of about 55 $MN\,m^{-2}$ to the minimum fracture strengths of each of the low strength batches to bring them on to the line for the flaw sizes observed. Whilst it is inconceivable that anything approaching this could be generated by thermal stresses during cooling and, intuitively at least, it seems unlikely that such large stresses could exist at 1650° C when the creep rate, even of doped UO_2, is high, the fact that rings were often found to be cracked after sintering, coupled with the relatively small flaw size and the absence in the batches of the large fissures, does argue, qualitatively, in favour of the existence of some residual stress. The relatively large spread of the measured strengths (Table III) also reinforces this argument.

The difficulties of obtaining uniform powder or granule packing during the pressing of thin-walled ceramic bodies are well known. The effects of any non-uniformity will be at their worst when granules are not deformed during pressing and in these circumstances the conditions for the formation of fissure-like pores are at their most favourable. If this is indeed the true explanation of our results it is clear that great care needs to be taken in the fabrication of specimens such as these and possibly too, that the cylinder height: wall thickness ratio needs to be reduced.

It is interesting to compare the present results with those obtained by Evans and Davidge [8] on undoped UO_2. They determined the bend strengths and energies for fracture initiation γ_i, for specimens having mean grain sizes of 8 and 25 μm. The minimum strengths quoted for these were approximately 150 and 115 $MN\,m^{-2}$ and the values for γ_i were 7 and 4 $J\,m^{-2}$ respectively. The largest pores found in each material were 50 μm in diameter. The energies for fracture initiation for the present materials were not determined but

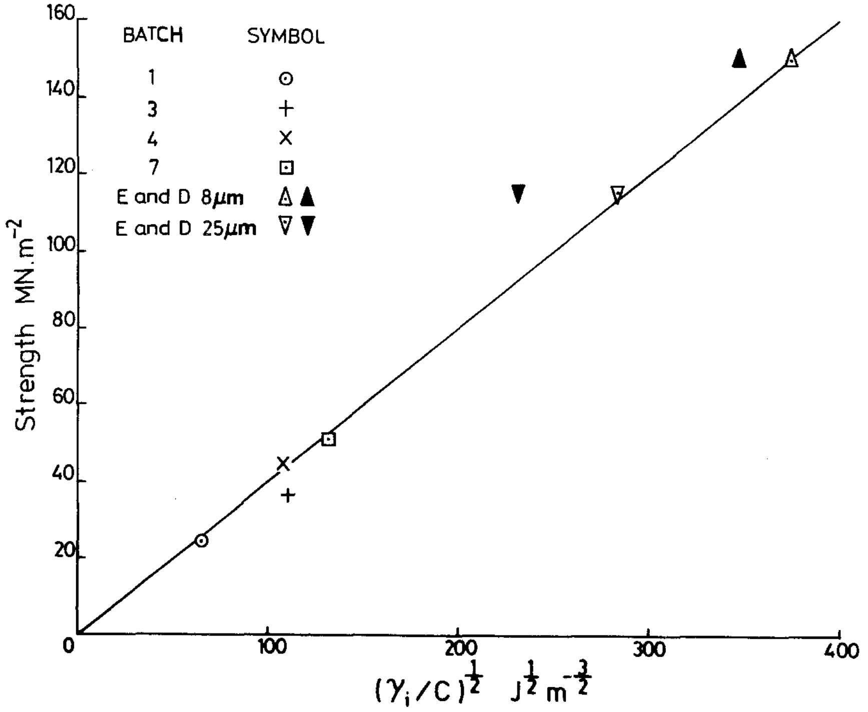

Figure 4 Minimum strengths as a function of $(\gamma_i/c)^{\frac{1}{2}}$.

batches 1, 3, 4 and 7 are considered to have approximately the same value. These materials are similar in grain size and density to the 8 μm material tested by Evans and Davidge and, therefore, should have a similar value for γ_i. It is found that the minimum strength value for this material will fit the linear relationship (Fig. 3) with the flaw size taken as 50 μm. This can be seen in Fig. 4 where minimum strength is plotted against $(\gamma_i/c)^{1/2}$ for both the present results and those of Evans and Davidge. To do this, a value of 7 J m^{-2} has been assumed for the present results. It can be seen that the present results and those of Evans and Davidge are consistent when it is assumed for the latter that the flaw sizes are equivalent to the diameter of the maximum sized pores. However, Evans and Davidge consider that the necessary sharp end for propogation of a flaw is provided by a grain-boundary groove in the pore wall, which they consider would easily extend until it intersected the next grain. They thus consider that the flaw size should be taken as the pore diameter plus one grain diameter. The present results are not significantly altered if the grain diameters are or are not included, because the flaws are large compared with the grain size. However, those of Evans and Davidge are affected, and it can be seen from Fig. 4 that the results with the grain diameters included are not in such good agreement with the present results or for that matter between themselves.

The fracture surfaces of all our specimens showed that failure had occurred in a transgranular manner. A similar observation was made during the examination of both UO_2 and magnesia-doped UO_2 rings fractured in our earlier work [2, 5]. Evans and Davidge [8] report approximately 60% transgranular fracture in their 25 μm grain size UO_2 but only 30% transgranular fracture in their 8 μm material. It appears, therefore, that the proportion of intergranular fracture increases with fracture stress, possibly as a result of expending the higher stored energy.

The basis of the argument put forward here is that the minimum fracture strength of UO_2 with or without the presently added impurities can be explained in terms of the maximum flaw size, possibly coupled with the assumption of residual stress. This implies that the impurities at the levels employed, do not alter the energy for fracture initiation of the specimens.

Although calcium oxide added as a powder produced large pores, it is possible that the largest pores and fissures seen in all the specimens were the result of poor packing and/or deformation of the granules during pressing and not caused by the added impurities.

So far as we are aware most, if not all, of the published work on the effect of impurities has attempted to relate mean fracture strength to the presence and concentration of impurities. Thus Solomon [4] found that additions of silica reduced the mean fracture strength while additions of iron had a negligible effect. Although the present work generally substantiates this conclusion, the mean fractures stresses for UO_2, UO_2/Fe and UO_2/SiO_2 being 69.1, 61.2 and 40.8 MN m^{-2}, respectively, it is thought that this is fortuitous.

5. Conclusions

The ring test, in which the tensile stress imparted to the specimen is much more unform over the specimen cross-section than in the three-point bend test, was developed since it was expected that the bend test by virtue of the stress distribution, was likely to give unrealistically high values of fracture strength. The present work indicates that if minimum strength values are taken, the two tests can yield comparable results which can be related to the maximum flaw size. It is reasonable to expect any relationship between strength and flaw size to hold only in the absence of any significant residual stress. Failure to meet this condition may explain why some of the batches of material examined in the present work have anomalously low strengths.

Silicon, calcium and iron all occur as major impurities in sintered UO_2 pellets. An investigation into their possible effect on strength has led to the conclusion that the silicon and calcium do not alter the energy for fracture initiation and in the form in which they occur naturally they are not expected to produce serious flaws. The behaviour of iron in the present work was obscured, it is thought, by the presence of residual stress. However, considering the size and number of inclusions that occur naturally, it should not have a significant effect on strength.

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