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Argonne National Laboratory

MECHANICAL PROPERTIES OF URANIUM COMPOUNDS

by

C. R. Tottle

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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OF URANIUM COMPOUNDS

by

C. R. Tottle

Metallurgy Division

Metallurgy Program 9.5.11

Portions of this material have appeared in
ANL-7000, pp. 97-98

November 1965

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	7
INTRODUCTION.	7
EXPERIMENTAL PROCEDURE	8
URANIUM DIOXIDE	9
Preparation of Samples	9
Testing Conditions	10
Load-deflection Tests	11
Discussion of Results	14
Mechanism of Deformation.	16
Effect of Atmosphere	23
Relaxation of UO_2 at High Temperatures.	25
URANIUM SULFIDE	25
Load-deflection Tests	26
Discussion of Results	26
URANIUM PHOSPHIDE	29
Load-deflection Tests	29
Discussion of Results	30
BINARY SYSTEMS	30
CONCLUSIONS.	31
PROPOSALS FOR FURTHER WORK	32
ACKNOWLEDGMENTS	32
REFERENCES	33

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Tungsten Tools for Bending Specimens.	9
2.	Close-up of Furnace with Specimen in Position	9
3.	Load-deflection Curves for Slow Strain at 25, 1000, and 1250°C	12
4.	Load-deflection Curves for Fast, Medium, and Slow Strain at 1500°C	12
5.	Load-deflection Curves for Medium and Slow Strain at 1750°C .	13
6.	Load-deflection Curves for Medium Strain at 1900°C	13
7.	Maximum Stress and Total Strain vs Temperature for High- density UO_2	13
8.	Young's Modulus of Elasticity vs Temperature for Uranium Compounds	15
9.	Bars Bent at 1750°C, Slow, Medium, and Fast Strain, and Fractured after Fast Strain	15
10.	Fracture Face after Testing at 25°C.	17
11.	"Necklace-type" Porosity	18
12.	Crack Joining Pores	18
13.	Crack Opened Out and Progressing at Tip at 25°C	18
14.	Fracture Face after Testing at 1500°C	19
15.	Progress of Cracking Mechanism at 1500°C	20
16.	Several Voids Joined as a Lenticular-shaped Crack	21
17.	Cracks on the Tensile Face of a Specimen Deformed at 1750°C, but Not Broken	21
18.	Deformation at 1750°C.	22
19.	Deformation at 1900°C.	22
20.	Agglomeration of Voids Toward Triple Points at 1900°C	22
21.	Widmannstätten Pattern in US and UOS Eutectic	28
22.	Strength and Ductility of Uranium Compounds	28
23.	Etch Pits in US	29
24.	Polygonization in US above 1250°C.	29

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Deformation of UO_2 at 25, 1000, and 1250°C.	11
II.	Deformation of UO_2 at 1500, 1750, and 1900°C in Vacuo	12
III.	Tests in Varying Atmospheres on UO_2 at 1500°C	23
IV.	Creep Tests on UO_2 in Vacuo	25
V.	Mechanical Properties of US at Medium Strain Rate	27
VI.	Mechanical Properties of UP and 62% UO_2 -38% UP Mixture . . .	30

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MECHANICAL PROPERTIES OF URANIUM COMPOUNDS

by

C. R. Tottle

ABSTRACT

Mechanical tests, in which four-point loading was employed in bending, have been carried out, at temperatures from room temperature to 2000°C, and mainly in vacuo, on uranium compounds with oxygen, with sulfur, and with phosphorus.

UO₂ has been most fully explored, and a brittle-ductile transition shown to exist between 1250 and 1500°C. The effect of strain rate, atmosphere, density, and surface condition has been outlined.

US has been tested in forms incorporating UOS and/or UO₂ as impurities. The ductile transition occurred around 1000°C for UOS-bearing material, and around 1250°C for US containing UO₂.

UP containing about 1% UO₂ was tested in the same way as US and was shown to have a transition around 1250°C.

UO₂ remained stronger than the others at all temperatures except 1000°C, but was less plastic. US containing UOS was consistently the weakest material. The temperature dependence of stress was remarkably similar in all the materials between 1250 and 1750°C.

Specimens of all three compounds were (under appropriate conditions) bent to deflections exceeding 2.5 mm around the inner knife edges 6 mm apart and around the outer knife edges 30 mm apart.

Proposals are made for future work on ceramic materials of this type.

INTRODUCTION

Brittleness is a relative term for a mechanical property much abused by engineers and metallurgists, since it is meaningless unless stated in context with conditions of temperature and rate of straining.^{1,2} Many metals and alloys (e.g., tungsten, steels) break with a brittle fracture under conditions of impact loading and/or at low temperatures, but are ductile under

the conditions of their application. Ceramic materials are normally brittle at room temperature, and even at moderately high temperatures. Many of them also exhibit a combination of low thermal conductivity and medium to high thermal expansion, leading to strains on thermal cycling, and consequently, a reputation for brittleness and low strength. In fact, most compounds of metals with a single nonmetallic element (these compounds embrace most of the materials we now refer to as ceramics) are, intrinsically, of relatively high cohesive strength, leading to high melting point and mechanical strength. They become ductile, however, and often retain a considerable strength at temperatures exceeding the melting points of all but the high-atomic-number transition metals and most alloys.

Little evidence in support of these favorable properties has been published, for two reasons: first, a reluctance to acknowledge a "brittle" material in any other light; and second, the difficult techniques required for very-high-temperature, atmosphere-controlled tests. Uranium compounds, having only restricted application in nuclear-energy projects, and being toxic in addition, have received less attention than some other ceramic materials.³ This work describes a technique suitable for uranium compounds with oxygen, carbon, silicon, nitrogen, sulfur, phosphorus, and binary systems of these.

EXPERIMENTAL PROCEDURE

In assessment of true ductility, tensile properties are of greater interest than tests in compression, but the manufacture of suitable specimens, and of machine grips to hold them during the test, is extremely difficult with ceramic materials.^{4,5} Bending in four-point loading requires simple tools and geometrically simple specimens, and produces failure originating in the tensile face and propagating through the section.⁶ This method of testing was therefore adopted, the tools used being made of tungsten, which is compatible with most uranium compounds up to 2000°C. Figure 1 is a drawing of the tools. A testing machine of 4536-kg capacity, fitted with a high-vacuum furnace incorporating a tungsten-mesh heating element, was available. Figure 2 shows the setup of heating element, specimen, and tools. The furnace was capable of 2350°C maximum temperature, and readily attained pressures of 2×10^{-6} Torr. Valves were provided to admit other atmospheres or allow circulation of gas through the furnace.

The testing machine was fitted (initially) with a dial gauge, bearing on the crosshead, and (later) with an encapsulated differential transformer, also bearing on the crosshead and connected to an X-Y recorder. It was possible to measure deflections by either of these devices, and to record this measurement against the load. The machine also incorporated a

constant-load regulator, which was used in appropriate tests. The elastic strain in the tools and grips was limited by the low loads required to bend the ceramic specimens. No evidence of plastic strain in these members was evident after 200 tests.

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Fig. 1. Tungsten Tools for Bending Specimens

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Fig. 2. Close-up of Furnace with Specimen in Position

URANIUM DIOXIDE

Preparation of Samples

A batch of depleted UO_2 powder (manufactured by Kerr-McGee) of oxygen-uranium ratio initially 2.06 was available, with a purity better than 99.95%, as determined by emission spectrographic analysis. The average particle size was determined by the Fischer permeability method to be 0.5 micron. Frequent checks on the powder particle size showed no change as the container was emptied.

Bars were cold-pressed in a hardened steel die to a size $6.35 \times 0.8 \times 0.8$ cm, under a load of 5445 kg. Two-percent Carbowax 4000

(polyethylene glycol), dissolved in hot water, was added to the powder as a binder initially, but later was eliminated. The bars were hydrostatically pressed at 3867 kg/cm^2 after removal from the die, sintered in hydrogen at 1750°C for 4 hr, and then slowly cooled in hydrogen. Densities up to 96% theoretical were normally achieved. Lower densities were obtained by varying the sintering temperature or the rate of heating before and after removal of the Carbowax binder.

All specimens were measured by micrometer for uniformity, and for the dimensions at the center span of the knife edges where fracture would occur. Density measurements were made by weighing in air and in carbon tetrachloride. Similar measurements were made after mechanical tests, suspending any fractured specimens in a wire stirrup so that no bubbles could accumulate in the fractured surface. (This method tends to give slightly high results if CCl_4 penetrates into open pores.)

Before being tested, representative samples were examined microscopically to check on grain size, uniformity of porosity, and any other features.⁷

Testing Conditions

The principal variables adopted were temperature and strain rate. Tests were made at room temperature, 1000, 1250, 1500, 1750, and 1900°C . The latter temperature proved to be the maximum permissible with UO_2 , since volatilization was occurring reasonably rapidly, and testing time was limited to 20 to 30 min, thereby eliminating the use of very slow strain rates.

The testing machine was fitted with controlled straining gear. At lower temperatures, due to the high-strength behavior coupled with low deformation of the UO_2 , a rate of loading was in fact being measured and was so recorded. At higher temperatures, the load rate was modified by the plastic deformation, and hence a strain rate was actually measured and recorded in addition. The same three rate settings of the machine were used throughout and referred to as slow, medium, and fast. They represented the lowest three rates calibrated on the machine in the ratio 1:10:20.

Experiments were also conducted with specimens of variable density, and after removal of the surface skin, on the tension side, by grinding. These experiments are reported separately, since it was considered unnecessary to duplicate all other tests with these added variables. Most of the tests were conducted in vacuum, but other atmospheres were employed in specific tests.

Precautions taken to avoid external influences on the mechanical properties included the following:

1. Handling of specimens by tongs or gloves after sintering, and storage in a desiccator, to avoid moisture on the surface.

2. Slow heating to test temperature, not exceeding 20°C/min, to avoid thermal shock.
3. Allowing a minimum of 5 min at test temperature before commencing load application.
4. Repeated checks on zero load point of testing machine.
5. Repeated checks on alignment of tools and wear on knife edges, with replacement of the latter as required.
6. Regular cleaning of optical pyrometer sight glasses, heat shields, tools, grips, and furnace casing.

Load-deflection Tests

The results of the load-deflection tests are presented in the form of tables, showing the modulus of rupture where fracture occurred (otherwise the maximum stress), expressed as a mean value for each batch of test conditions, with a standard deviation. A mean value and standard deviation for density are also given. Relevant loading or strain rates are mean values for the batch. To emphasize the trend in behavior from brittle to ductile, Table I refers to brittle behavior, and Table II to ductile. To illustrate the variation in load-deflection curves obtained with temperature and strain rate, Figs. 3-6 are taken from specimens closest to the mean values recorded in the tables.

TABLE I. Deformation of UO_2 at 25, 1000, and 1250°C

Number of Specimens	Density, g/cc		Modulus of Rupture kg/cm ²		Mean Load Rate, g/sec	Mean Total Strain, mm	Temperature, °C	Atmosphere
	Mean	Standard Deviation	Mean	Standard Deviation				
5	10.58	0.009	843	128.0	68.0	-	25	Air
5	10.44	0.07	598	37.2	68.0	-	25	Air
4	10.07	0.01	433	50.8	117.9	-	25	Air
5	10.26	0.025	943	18.2	680.4	-	25	Air
5	10.64	0.001	1511	91.4	86.2	0.13	25	Vacuum
4	10.59	0.005	1480	91.4	285.7	0.11	25	Vacuum
4	10.55	0.003	1239	92.0	63.5	-	1000	Vacuum
4	10.60	0.01	1306	352	204.1	0.18	1000	Vacuum
5	10.51	0.016	1044	81.7	1115.9	-	1000	Vacuum
5	10.60	0.01	1759	98.2	27.2	0.28	1250	Vacuum
2	10.62	0.005	1624	53.0	195.0	0.18	1250	Vacuum
5	10.61	0.005	1317	111.6	548.8	0.20	1250	Vacuum
5	9.85	0.24	1234	93.8	199.6	0.23	1250	Vacuum
4	10.23	0.05	792	134	426.4	0.13	1250	Vacuum

Figure 7 summarizes the relationship between maximum stress and corresponding total strain at each test temperature, for the three rates of straining, and for high-density specimens only.

TABLE II. Deformation of UO_2 at 1500, 1750, and 1900°C in Vacuo

Number of Specimens	Density, g/cc		Maximum Stress, kg/cm^2		Mean Strain Rate, $\text{mm}/\text{sec} \times 10^4$	Mean Total Strain, mm	Mean Load Rate, g/sec	Temperature, °C
	Mean	Standard Deviation	Mean	Standard Deviation				
5	10.45	0.05	1017	95.2	2.2	0.51	19.5	1500
4	10.58	0.01	1110	76.0	11.9	0.38	172.4	1500
4	10.60	0.07	1213	109.5	19.8	0.34	376.5	1500
4	10.34	0.05	1245	146.0	9.4	0.41	136.1	1500
5	10.04	0.10	1306	156.0	16.0	0.18	444.5	1500
5	9.86	0.04	916	118.0	1.9	0.86	11.3	1500
5	9.65	0.10	1013	165.0	14.5	0.20	439.9	1500
5	10.50	0.07	479	99.7	3.0	0.89	8.2	1750
5	10.44	0.15	709	156.0	12.4	1.07	54.4	1750
5	10.61	0.002	1655	534.0	29.0	2.48	95.3	1750
4	10.60	0.01	752	94.9	13.5	1.78	31.8	1900
4	10.60	0.02	914	35.6	30.9	3.56	77.1	1900

41037

Fig. 3. Load-deflection Curves for Slow Strain at 25, 1000, and 1250°C

41033

Fig. 4. Load-deflection Curves for Fast, Medium, and Slow Strain at 1500°C

Fig. 5
Load-deflection Curves
for Medium and Slow
Strain at 1750°C

41036

Fig. 6
Load-deflection Curves for
Medium Strain at 1900°C

41034

Fig. 7
Maximum Stress
and Total Strain vs
Temperature for
High-density UO_2

41035

No results are included, either in tables or figures, where fracture occurred outside the span of the inner knife edges.

Discussion of Results

As shown in Fig. 7, and detailed in Tables I and II, UO_2 is by no means brittle at high temperatures. Above 1250°C , a substantial increase in the deflection and, usually, a corresponding drop in the maximum stress were obtained with each rise in temperature. Up to 1250°C (the brittle range), a slower strain rate produced a higher modulus of rupture, presumably due to the increased time for relaxation in the highly strained areas of the crystal lattice or around internal pores. Beyond this point, however, the situation completely reversed, and higher strain rate produced increased maximum stress. Furthermore, the fastest rate used exerted its maximum effect at 1750°C , whereas this occurred at 1250°C for the two slower rates employed. Deflections increased steadily with rise in temperature, and above 1500°C with higher strain rate. At 1750°C , the ratio of maximum stress to deflection was approximately constant, whatever the strain rate, indicating an optimum plasticity for relaxation.

Previously published work on UO_2 concerned, in the main, testing at room temperature in air and, obviously, at higher temperatures in vacuum or inert atmosphere.^{7,8} The present work indicated that vacuum testing at room temperature produced a considerable increase in strength over air testing (Table I), and that at 1000°C , the previously reported improvement in strength was not maintained when the same atmosphere is used at both temperatures. The explanation must involve the moisture present in air, producing stress-corrosion effects at the crack tip, since oxidation is too slow at 25°C to account for the difference. No change in stoichiometry could be detected in any specimens, as determined by the technique of oxidation to U_3O_8 .

Tables I and II indicate that a decrease in density produced a distinct drop in strength at temperatures below 1500°C . At 1500°C , a small decrease in density produced little change, but a large decrease caused a definite loss of strength, within the limits of experimental error. The mechanism of deformation must change with temperature, and therefore the effect of porosity must also change.

Figures 4 to 6 show that load-deflection curves measured above 1250°C (where UO_2 becomes more plastic) closely resembled those for conventionally ductile metals. The elastic range was clear and definite; both slope (modulus) and elastic limit increased with increases in temperature. Crude though these measurements were by normal standards of measurement of elastic modulus, the values of E were within 5% of published figures³ (see Fig. 8). The yield point became more definite at 1500°C , but

42211

Fig. 8. Young's Modulus of Elasticity vs Temperature for Uranium Compounds

be detected. Audible clicks often accompanied the yielding, frequently deceiving the operator into believing that fracture had occurred. In steel, such clicks have been ascribed to twinning and cleavage fracture, restrained by grain boundaries.⁹

The type of curvature produced in the bars at the higher temperatures is illustrated in Fig. 9. In the author's opinion, the design of special tools, to bend specimens around a suitable large radius, would make possible 180° bends in UO_2 at 1750°C and above.

Fig. 9. Bars Bent at 1750°C , Slow, Medium, and Fast Strain, and Fractured after Fast Strain

Mechanism of Deformation

Measurement of density after test showed a decrease greater than experimental error. Completely fractured specimens had decreased by 1.5 to 8% in density, the faster strain rate and higher temperatures having caused the greatest change. Unbroken samples decreased less, depending on how far cracks had penetrated through the section before fracture. A small crack, extending only 1.25 mm or so into the section, produced about 0.5% change, the variation increasing to the point where 95% penetration decreased the density in direct proportion to that of a complete fracture. Low initial density gave rise to the greatest change below 1250°C, and the smallest change at higher temperatures. At 1900°C, above the initial sintering temperature of the UO_2 , some volatilization of the material occurred, but a much greater densification by migration of pores. A net increase in density (about 0.3%) resulted.

In metals and alloys, separate stages may be recognized in the fracture process, whether ductile or brittle, as follows:

1. Deformation, large or small, leading to voids on an atomic scale.
2. Nucleation of a crack or cracks at such atomic-sized voids.
3. Propagation of the crack or cracks.
4. Separation of the crack surfaces, becoming complete at final fracture.

Stage 1 depends on the deformation modes of the material, the feasibility of cross slip, and interference of dislocation movements by slip bands, subboundaries, grain boundaries, impurities, vacancies, etc. Stage 2 is largely governed by the situation created in Stage 1 reaching a critical size or stage of development. Stage 3 involves deformation, or the absence of it, and its velocity largely governs the concept of brittle or ductile fracture. Stage 4 depends on the inherent properties of the material, the progress of Stage 3, and the stressing conditions.

Ionic solids do not differ so markedly from metals in this respect, and similar arguments have been used in the past to explain fractures in them.^{2,9,10} A major difference, however, is the greater influence of existing voids and cracks known to be present in polycrystalline ceramic materials. Brittle behavior has often been assumed to follow simple propagation of a crack initiated at such a void, with or without a small amount of plastic deformation. The rate of application of load must have some influence on the time available for slip to take place, and therefore on whether such phenomena as yield points are observed. In the present work, very little plastic flow occurred at room temperature, and a finely textured fracture was observed (see Fig. 10), partly intercrystalline, partly cleavage.

40853

X16

Fig. 10. Fracture Face after Testing at 25°C

Carniglia¹¹ has proposed a model (for MgO, Al₂O₃, and BeO) in which crack initiation is largely dependent on the grain-boundary conditions, and shear within the plane of a grain boundary takes place more readily than yield within grains at low to relatively high temperatures. He emphasizes the role of grain size and of purity (less impurities raise the boundary-yield stress). The present work on UO₂ supports much of this hypothesis, but emphasizes more the role of porosity.

In the present work, most pores were found to be uniformly distributed at triple points in the grain boundaries, in a roughly hexagonal symmetry, as would be expected from their origin as

cusps at particle junctions. The grain size of all specimens tested was between 10 and 20 microns, so that grain growth of 20 to 40 times occurred at the sintering temperature. This type of porosity (see Fig. 11) was termed "necklace" porosity in view of the distribution and pore shape. Numerous examples were obtained, at room temperature, of microscopic cracks spreading from these pores and propagating mostly along grain boundaries, but occasionally across a grain where the conditions were obviously favorable (see Fig. 12).

Subsequent development of such cracks produced an elongated macroscopic void of considerable dimensions, with an enlargement of the central portion. Figure 13 shows one-half of such an elongated void. Further advance of the macroscopic crack continued by microscopic enlargement and elongation of pores similar to those of Fig. 12 and can be seen following a grain-boundary path in Fig. 13. Some pore growth took place on each side of the crack and the almost spherical central void, but the triaxial stresses are highest at the crack tip and therefore influence the direction of the main propagation.

Specimens tested at 1000 and 1250°C followed a similar behavior to that at 25°C and so characterized the brittle range. After polishing many sections from these tests, one became aware that only one or two microscopic cracks formed at 25°C and that these became the basis of the fracture mechanism. At 1000°C, and further at 1250°C, a greater, but limited number of such cracks could be found, close to the fracture. At the higher temperatures, the widening of the cracks, and the appearance of

the enlarged voids at their extremities, suggested increasing plasticity, though the same fundamental mechanism still operated to failure.

40857

X1300

Fig. 11. "Necklace-type" Porosity

40859

X1300

Fig. 12. Crack Joining Pores

40855

X130

Fig. 13. Crack Opened Out and Progressing at Tip 25°C

In the ductile range, i.e., above 1250°C, the fractured faces indicated much greater plasticity near the tensile face in the early stages of crack propagation, leading to a more fibrous appearance. At 1500°C, the fibrous portion occupied perhaps one-third the area, the remainder being similar in texture to those obtained at 25 to 1250°C (see Fig. 14). As temperature increased, the final parting of the two faces also involved a smaller proportion of the cross-sectional area. At 1750°C, and more so at 1900°C, the fibrous fracture covered two-thirds or more of the area, and at 1900°C an extremely thin skin remained at final parting. Much of the load applied at 1750 and 1900°C was involved in separation of the two faces, and tests could be discontinued at any point, even at 1250°C, to section the specimen for examination of cracks in formation or propagation.

40581

X17

Fig. 14. Fracture Face after Testing at 1500°C

leading to the fibrous texture and crumbling nature of the material close to the fracture. A well-developed small crack in the later stages is shown in Fig. 16, and cracks on the tensile face of an unbroken specimen are shown in Fig. 17.

Obviously, the time available for elongation and distortion of the pores before rapid crack propagation occurs must affect the measure of plastic deformation observed. The stress concentrations around a suitably oriented pore will lead to yielding in the boundary, or in the grains, on either side. In the boundary, there will be a tendency to produce a sharper stress concentration, leading to crack nucleation and propagation (see Fig. 18). This could also occur in the grain if one of the many mechanisms described for metals^{2,9,10} is involved, but the chances of this seem to be far less than that of boundary nucleation. The model described by Hasselmann¹² would appear to be far more pertinent in this case, from the microstructures observed. Nevertheless, one specimen, deformed at 1900°C, showed cracks apparently following parallel slip planes in one grain, and often commencing at etch pits, probably the site of some dislocation pile-up, creating an atomic-size void (see Fig. 19). The 1900°C temperature also produced some unusual diffusion effects, such as the agglomeration of pores towards selected triple points, no doubt accelerated by the applied stress (see Fig. 20).

The cracking mechanism above 1250°C followed a similar general pattern to that below the transition from brittle to ductile behavior, but was much more confined to grain boundaries and involved a greater degree of enlargement of pores. Figure 15 shows the enlargement in its early stages, the joining up, the subsequent elongation of these connections, and finally, the formation of a definite void forming part of a propagating crack. Although many pores enlarge, as shown in Fig. 15(a), not all pores progress to stages (b) and (c), and fewer still progress to the shape shown in Fig. 15(d). The plasticity observed, however, is the summation of all these effects, at all stages; and final fracture occurs by gradual separation of several possible void or crack sites,

(a) Enlarged pores close to tensile face

40860

X1300

(b) Pores connecting up

40861

X1300

(c) Enlargement of connected pores

40862

X1300

(d) Enlarged pore becomes a distinct void

40863

X1300

Fig. 15. Progress of Cracking Mechanism at 1500°C

40864

X250

Fig. 16. Several Voids Joined as a Lenticular-shaped Crack

40674

X25

Fig. 17. Cracks on the Tensile Face of a Specimen Deformed at 1750°C, but Not Broken

41009

X260

Fig. 18. Deformation at 1750°C. (Voids opened up near tensile face.)

41010

X1300

Fig. 19. Deformation at 1900°C. (Cracks apparently following slip planes and including etch pits.)

41011

X1300

Fig. 20. Agglomeration of Voids Toward Triple Points at 1900°C

The considerable decrease in density observed in completely fractured specimens and the much smaller decrease in density observed in unbroken or only partially fractured ones, suggest that energy stored up at the stress concentrations was released suddenly in the final stages of fracture. Low-density specimens (less than 10.4 g/cc) possessed larger pores initially than high-density ones, but in much the same number and distribution. The stress system around them would therefore be less concentrated, owing to the greater radius of curvature. Porous specimens therefore deformed more slowly than others, even at fast strain rates. Above

1500°C, all specimens deformed more readily at fast strain rate, so that yielding must have occurred more rapidly than crack propagation, the difference increasing with increases in temperature. Below 1500°C, the slower the strain rate, the more time was available for stress relaxation at concentrations, and a higher breaking load was recorded in spite of the brittle nature of the material.

Specimens from which the surface skin had been ground away to a depth of 1.3 mm on the tensile face were tested at 1500 and at 1750°C, using a medium strain rate. The ductility and maximum stress increased by 10% at 1500°C and 50% at 1750°C (see Table III). Since the surface skin contained a lower volume of pores than the interior, the ground face was capable of increased stress relaxation before crack propagation became rapid; hence an increase in both ductility and maximum stress was possible, confirming the hypothesis of porosity influence.

TABLE III. Tests in Varying Atmospheres on UO₂ at 1500°C

Number of Samples	Density, g/cc		Maximum Stress, kg/cm ²		Mean Strain Rate, mm/sec x 10 ⁴	Mean Total Strain, mm	Mean Load Rate, g/sec	Atmosphere	Remarks
	Mean	Standard Deviation	Mean	Standard Deviation					
4	10.59	0.01	859	16.6	12.2	0.38	149.7	Helium 1-5 mm	Moisture present.
6	10.52	0.03	932	43.2	9.8	0.33	149.7	Hydrogen 1-5 mm	Trace of moisture due to reaction.
5	10.47	0.004	793	48.7	12.0	0.18	303.9	Dry, flowing hydrogen	Low density.
5	10.62	0.001	1568	88.9	7.5	0.43	145.2	Dry, flowing hydrogen	High density.
4	10.61	0.0001	1970	450	9.1	0.36	176.9	Dry, flowing hydrogen	Ground on tensile face.
3	10.62 ground to 10.60	0.005	1228	72.2	10.4	0.43	-	Vacuum	
2	10.50 ground to 10.48	0.05	1278	94.9	13.21	1.98	-	Vacuum	1750°C

A limit was reached with porous specimens when the pores occupied such a large proportion of the cross section that the load-bearing surface area was reduced drastically, and low strengths resulted. This point was well-covered by Hasselmann.¹²

Effect of Atmosphere

Tests were made in atmospheres of helium and hydrogen at high temperatures. The moisture content of gases compressed in cylinders increases as the pressure falls, and a drying train of molecular sieve material and liquid-nitrogen traps was used on the helium supply. Tests showed that at least 10 ppm of moisture were still present after this treatment, and time did not allow the drying system to be developed. Hydrogen was available in pure form through a palladium purification valve, and moisture could not be detected in the final gas stream.

The moisture present in the helium produced definite changes in the mechanical properties of UO_2 . A stagnant hydrogen atmosphere produced a similar effect, due to reduction of oxide films inside the furnace. A clean-up procedure with pure hydrogen, followed by purging with fresh hydrogen, largely eliminated this, but flowing hydrogen appeared to sweep out any moisture much more effectively. Whatever the atmosphere, the presence of moisture caused a general decrease in yield point and maximum stress, but an increase in ductility.

Pure flowing hydrogen, free of moisture, and clean surfaces inside the furnace, raised the maximum stress, in high-density samples, without loss of ductility. Under fast rates of strain, the ductility at 1500°C in pure hydrogen was the highest ever recorded.

When the density was low, pure hydrogen and moisture-free conditions resulted in a drop in ductility but preserved the high strength. These results are summarized in Table III.

One possible explanation of the effect of hydrogen or moisture is as follows: The presence of water invariably lowers the breaking strength, even at room temperature (see portions of Table I for tests in air). At high temperatures, the ductility increases in spite of the loss of strength. The stress relaxation around pores and the stress system at a propagating crack tip, in particular, may be involved in the change in ductility. It is suggested that hydrogen is formed by dissociation of the moisture at the surface of the sample (more rapidly when hot) and diffuses into the UO_2 lattice in either the atomic or ionic state. Oxygen formed at the same time enters the lattice also, creating hyperstoichiometry near the surface. The hydrogen atom being smaller, the hydrogen will diffuse more rapidly into the lattice and interfere with dislocation movements, either by increasing the frictional stress, or by occupying vacancies that normally assist movement of U-O pairs in slip. The strength is increased by the hydrogen, and the ductility is increased by the oxygen, since hyperstoichiometric UO_2 is much more plastic than the stoichiometric material. Since the oxygen is confined to a smaller depth than hydrogen in the diffusion into the sample, the strength factor should be more apparent than the increased plasticity. The higher the temperature, the more rapid the diffusion of both hydrogen and oxygen, and the greater the increase in strength and ductility.

Atomic hydrogen produced at the surface of a sample by dissociation of water should enter the lattice relatively easily. Dissociation of molecular hydrogen at the surface requires greater energy. This dissociation will be slow in the absence of moisture and will only be increased by higher temperatures or greater surface area. To test this premise, samples were tested in pure dry hydrogen after a portion of the tensile face was ground off to expose porosity in the interior. The results confirmed the hypothesis

of increased surface for dissociation. This may also explain why low-density specimens are more affected by hydrogen than high-density ones, since porosity is greater close to the surface having low density.

Relaxation of UO_2 at High Temperatures

As a final demonstration of the relaxation properties of UO_2 , one sample was bent to a deflection of 0.76 mm under medium rate of straining at 1750°C , cooled to room temperature, inverted in the tools, and straightened by rebending at 1750°C under the same conditions. This procedure was carried out ten times, i.e., five complete cycles. Apart from increased indentation by the knife edges, no change was observed in the specimen on completion of the test. Examination of the microstructure revealed a large increase in the number of etch pits in the grains, and in the number of planes characterized by the pits. The dislocation density had obviously increased, probably by an order of magnitude.

Attempts were made to carry out creep tests, while using the constant-load device on the testing machine. This failed to function reliably enough to encourage overnight runs, and the absence of an extensometer made the recording of deflection-time curves difficult. These tests were abandoned for the time being, but served to show that slower rates of straining produced even greater relaxation than was expected, even at 1000°C . The only results of meaning are included in Table IV.

TABLE IV. Creep Tests on UO_2 in Vacuo

Temperature, $^\circ\text{C}$	Density, g/cc	Load, kg	Total Strain, mm	Time, hr	Minimum Deflection Rate, mm/mm/hr
1000	10.61	41	0.24	6	1.22×10^{-4}
1250	10.62	41	0.81	54.5	2.69×10^{-4}

URANIUM SULFIDE

Previous work on the preparation and properties of uranium monosulfide has been reported by Shalek.¹³ The process described was still in use, and several 500-g batches were produced for testing. One batch of material made some time before was also available and differed in composition because of slight oxidation of the powder. All batches were homogenized at 1850°C , crushed and sieved to -100 mesh, and finally ball-milled.

Forming was carried out in the same die as that used for UO_2 specimens, at 6804 kg load. A binder of 1% stearic acid was found to be suitable and essential. Sintering was performed in vacuo at 1800 to 1850°C, for 2 hr. Densities of 98% theoretical were obtained after the first trials.

The newly manufactured material contained oxysulfide (UOS), determined by the residue extraction method and X-ray diffraction to be approximately 1.5 w/o. No UO_2 was detected in this material. The older batch of material contained approximately 2.6 w/o of residues of which 2.3 w/o was UO_2 and 0.3 w/o was UOS.¹⁴ Tests were conducted on the material containing UOS and the material containing UO_2 to contrast the effect of both main impurities. The conditions applied were similar to those for UO_2 , with testing in vacuum, and over the same temperature range, but mainly with the medium rate of strain to limit the initial exploration.

Load-deflection Tests

The behavior of sulfide samples was found to be similar to that of UO_2 in general, but to vary with the impurities present. Load-deflection curves were similar in general shape; however, these deflections took place at lower temperatures.

US containing UOS fractured at lower stress than US containing UO_2 , but with only slightly lower deflection. Increase in temperature increased the maximum stress in both initially, but the maximum occurred at 1000°C for the UOS-bearing, and 1250°C for the UO_2 -containing, material. The ductility of the US + UOS batches increased dramatically above 1000°C, and similarly for US + UO_2 above 1250°C. In neither case was there a gradual change such as that noted for UO_2 , presumably because of the greater number of operative slip systems in the rock-salt lattice of US as compared with the fluorite type of UO_2 at these temperatures.

The strength of US fell more sharply with rise of temperature above that giving rise to the maximum stress value than for UO_2 , whether the impurity was UOS or UO_2 . The strength of US + UO_2 remained slightly higher (under all conditions) than for US + UOS. Table V summarizes the results in a similar way to those reported for UO_2 . At 1750°C, US showed little resistance to bending, and fracture was rapid.

Discussion of Results

The microstructure of US specimens indicated some of the reasons for the behavior at high temperature. As reported by Shalek, UOS was mainly present in the grain boundaries, having formed a liquid phase during sintering. Examination of the present specimens suggested a binary eutectic of US-UOS, along with primary UOS, in the boundaries, since large areas of light-gray UOS predominate both in narrow, filamentary boundaries and in

triple-point colonies. The Widmannstätten pattern referred to by Shalek^{13,15} was again evident, but the present work suggests this to be UOS-precipitated in the US grains as a result of a fall in solid solubility of UOS in US. The solubility is probably very small when in equilibrium at the sintering temperatures used (1800°C), since Shalek obtained much more of the pattern when using 1850°C for sintering. Etch pits have been produced in the present work and are shown to be unconnected with the Widmannstätten pattern. This largely disposes of the early suggestion on stacking faults.¹³ Baskin¹⁴ agreed that the original suggestion of Shalek¹³ with regard to the presence of UC has now been disproved also.

TABLE V. Mechanical Properties of US at Medium Strain Rate

Number of Samples	Density, g/cc		Maximum Stress, kg/cm ²		Mean Load Rate, g/sec	Mean Strain Rate, mm/sec x 10 ⁴	Total Deflection, mm	Temp, °C
	Mean	Deviation	Mean	Deviation				
UOS Impurity								
5	10.09	0.04	529	20.3	303.9	11.7	0.14	R.T.
4	10.12	0.05	1201	43.1	186.0	15.1	0.22	1000
3	10.21	0.02	895	55.3	59.0	10.7	1.27	1250
2	10.09	-	444	-	31.7	13.7	2.54	1500
3	10.31	-	265	66.7	-	-	3.17	1750
UO ₂ Impurity								
4	10.65	0.01	1069	155.9	258.6	6.9	0.18	R.T.
4	10.65	0.05	1215	189.1	213.2	6.1	0.23	1000
4	10.67	0.01	1382	44.9	195.0	5.8	0.25	1250
2	10.68	-	864	-	249.5	11.4	2.54	1500
2	10.69	-	324	-	-	-	3.10	1750

It would appear, therefore, that during sintering, US retains a small, solid solubility of UOS, but the main bulk of UOS, containing some dissolved US, remains as a liquid phase surrounding the US grains. During cooling, the US grains subsequently reject UOS in the Widmannstätten pattern, and the liquid phase breaks down into primary UOS plus the eutectic of UOS-US (see Fig. 21). Since UOS has a lower melting point (~1900°C) than that of US (2450°C),¹⁴ the strength of UOS at high temperatures will be lower than that of US. The presence of UOS in grain boundaries will cause grain-boundary sliding and considerable plasticity at a comparatively low temperature. This is precisely what happened to specimens containing UOS. However, the US itself must either have several available slip systems, or the presence of UO₂ affected the deformation mechanisms, since US with no grain-boundary UOS became quite plastic at 1250°C. The effect of UOS must therefore be a specific one, and Fig. 22 indicates that the displacement of the curve of strength against temperature for US is almost constant between 1250 and 1500°C, when UOS forms the grain boundary. Since US crystallizes with the rock-salt structure, it is extremely likely that it

exhibits several slip systems above 1250°C .^{2,10,11} At very high temperature (1750°C), the impurities in US appear to make little difference in the behavior, since the strength approaches zero as the temperature approaches the melting point of the basic material. In all samples of US, the number of etch pits in the microstructure increased after testing at high temperatures indicative of increased dislocation density (see Fig. 23). Polygonization of grains, inferring dislocation climb and an increase in the number of slip systems operative, was seen in many samples of US tested above 1250°C , as shown in Fig. 24.

42132

X260

42133

X650

Fig. 21. Widmannstätten Pattern in US and UOS Eutectic

42212

Fig. 22

Strength and Ductility of Uranium Compounds
(Vacuum Medium Strain)

42061

X650

42062

X1300

Fig. 23. Etch Pits in US

42131

X260

Fig. 24. Polygonization in
US above 1250°C

URANIUM PHOSPHIDE

Samples of UP, containing not more than 1 w/o UO_2 , had been prepared previously in the examination of several uranium compounds.¹⁴ The forming of square-section bars for bend-testing did not prove any more difficult than had been already found for UO_2 and US. A theoretical density of 96% was established, after early trials, in almost every bar. The material was prepared by hydriding uranium metal, followed by dehydriding and treatment with phosphine, PH_3 . The cold-pressing and sintering technique was followed as for US, with loads of 9072 kg and a sintering temperature of 1800°C.¹⁴

The microstructure of UP bars showed a fine grain ($15\ \mu$), with uniformly distributed fine UO_2 particles and some porosity in grain boundaries. (The material resembled UO_2 more than the US did.)

Load-deflection Tests

Testing was carried out in vacuo, at the same temperatures as for UO_2 and US. The results are shown in Table VI. The load-deflection curves

strongly resembled those of UO_2 at all temperatures of testing. It is obvious the UP does resemble UO_2 more than it resembles US, and the UP retains a higher strength, which is only slightly less than that of UO_2 , at high temperatures. The plasticity of UP is greater, however, than that of UO_2 , increasing steadily as temperature is raised, in a similar manner to US. Since UP does not evaporate quite so readily as UO_2 , the final tests were conducted at 2000°C , rather than at 1900°C as was used for UO_2 . Here the UP showed greater loss in strength, as would be expected from contrast of its melting point, 2610°C , against that of UO_2 , 2750°C .

TABLE VI. Mechanical Properties of UP and 62% UO_2 -38% UP Mixture

Number of Samples	Density, g/cc		Maximum Stress, kg/cm ²		Mean Load Rate, g/sec	Mean Strain Rate, mm/sec x 10 ⁴	Total Deflection, mm	Temp, °C
	Mean	Deviation	Mean	Deviation				
UP								
5	9.7	0.005	1234	46.1	213.2	6.2	0.20	R.T.
4	9.67	0.01	1556	198.2	195.0	5.8	0.27	1000
4	9.69	0.01	1413	144.2	145.2	7.9	0.46	1250
3	9.68	0.05	964	44.1	31.8	11.2	1.91	1500
3	9.63	0.01	637	-	20.0	14.1	2.54	1750
2	9.59	-	194	-	4.2	10.3	3.17	2000
UO ₂ /UP								
4	10.34	-	939	76.1	231.3	9.9	0.24	R.T.
3	10.25	-	970	45.3	163.3	12.2	0.43	1000

Discussion of Results

Examination of microsections after testing showed similar behavior to that of UO_2 at lower temperatures, i.e., the formation of enlarged voids, leading to crack propagation by both intergranular and transcrystalline modes. At higher temperatures, as in UO_2 , this mechanism still produced some deflection, but it was insufficient in quantity to account for the total plasticity measured. Again, the simplicity of slip in the grains became evident, by an increase in the number of etch pits and in the characteristic planes on which they occurred. The rock-salt structure of UP must obviously allow a greater number of operative slip systems to come into play, as compared with UO_2 . The ductility of UP is therefore partly caused by void enlargement and relaxation along boundaries, but at high temperatures, probably more as a result of slip within the grains. Figure 22 summarizes the properties of all the compounds tested.

BINARY SYSTEMS

In view of the differences shown to exist in the mechanical properties of the fluorite structure (UO_2) and the rock-salt type (UP and US), it became a matter of speculation as to the properties of combinations of these, as a possible means of providing "tailor-made" ceramics of predictable strength-ductility behavior.

Only one system was used in this work, as an initial exploration.¹⁶ Sixty-two w/o of UO_2 and 38 w/o of UP were mixed in a ball-mill and formed at 4500 kg load and sintered as for UP. The material displayed an interlocked angular particle shape of UP in a matrix of UO_2 , with some voids, probably as a result of differential thermal strains and reduced diffusion rate of vacancies.

The mechanical tests were carried out at room temperature and 1000°C only, and are summarized in Table VI and Fig. 22. It is obvious that the strength property of neither individual constituent is reached, but that plasticity is increased. The rise in ductility is greater than that produced by UOS in US, owing to the greater quantity of UP present, but the mechanism may be similar. The UP, with greater slip potential, forms the individual grains, and the UO_2 in the UP becomes a very thick boundary. The UP can slip to allow stress relaxation, but the UO_2 cannot develop its full strength. At higher temperatures, it may be possible to retain more strength and produce a uniformity of strength over a wide range of temperature.

CONCLUSIONS

1. Ceramic materials, as typified by three uranium compounds, can display appreciable ductility above a transition temperature, exactly as with metallic lattices.
2. The fluorite lattice of UO_2 gives rise to high strength, tensile stresses being greater than 650 kg/cm² up to 1500°C, with only slow deterioration above this temperature and up to 1900°C.
3. The deformation and strength of UO_2 are dependent on strain rate in addition to temperature. In the brittle range (below 1500°C), strength decreases with faster strain rate; in the ductile range (above 1500°C), plastic deformation also increases rapidly with fast straining, as does the strength. At 1750°C, UO_2 withstood stresses exceeding 1400 kg/cm².
4. At higher temperatures, the rock-salt lattice structures of UP and US convey a measure of increased plasticity, compared to UO_2 . The impurities present modify the behavior, particularly UOS in US, but this effect is probably less than that of the basic crystal lattice.
5. UOS lowers the maximum stress and increases the plasticity of US specimens by causing grain-boundary sliding. UO_2 has less effect on US and probably no more on UP when of the order of 2 w/o maximum.
6. All uranium compounds tested in bending exhibited an elastic range, a yield point, and a maximum stress in a similar manner to some ductile metals.

7. Porosity in UO_2 plays a vital role in the mechanism of deformation, and, as a result, some porosity is desirable in this material.

8. Atmosphere can modify mechanical properties by physico-chemical changes in UO_2 and no doubt would do so in UP and US.

9. A combination of two or more ceramic compounds may give rise to considerable modification of the properties of both constituents and suggests further development to secure optimum properties.

PROPOSALS FOR FURTHER WORK

1. The initial work on US and UP was confined to a single strain rate and did not include investigation of atmosphere or purity. These factors should be explored, particularly strain rate, before complete mechanical characterization of the materials can be stated.

2. Uranium compounds with other elements should be explored. The difference between UO_2 on the one hand, and UP and US on the other, warrants further exploration of UC, UN, and even the intermetallic compounds between uranium and arsenic, bismuth, antimony, etc.

3. The binary, and later ternary, mixtures of solid solutions of these compounds are likely to be of as great an interest as nuclear fuels as the alloys of uranium, and later, the same reasoning will apply to alloys and compounds of plutonium. To avoid unnecessary replication of projects, these should be investigated only with a thorough knowledge of the individual compounds.

4. Immediate projects might be limited to UC and UN and the binary systems of US-UC, UP-US, UO_2 -US, and UO_2 -UP.

ACKNOWLEDGMENTS

The author wishes to express his thanks to The University of Chicago and the Argonne National Laboratory for the opportunity to carry out this work, and to the Director of Metallurgy Division, F. G. Foote, and the Group Leader, Ceramic Engineering, J. H. Handwerk, for provision of facilities. He also acknowledges the valuable advice and assistance of his colleagues in the ceramic group, particularly that of G. M. Dragel.

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