

THE EFFECT OF SMALL ADDITIONS OF YTTRIA ON THE PLASTICITY OF URANIUM OXIDES AT 940° C

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The creep-in-bend behaviour of yttria/urania solid solutions containing 0.5 and 1 wt % Y_2O_3 , both in the fully reduced and oxidized states, has been studied at 940° C under a maximum fibre stress of 5000 psi.

The fully reduced solutions do not deform plastically under these experimental conditions, but yttrium additions to $UO_{2.18-2.20}$ reduce its plasticity.

The behaviour of the reduced solutions is explicable in terms of the hypothesis already advanced to explain improved plasticity in UO_{2+x} compared with stoichiometric UO_2 . Possible explanations for the behaviour of the oxidized solid-solutions are discussed.

Le comportement au fluage en flexion des solutions solides d'oxyde d'uranium et d'oxyde d'yttrium contenant de 0,5 à 1 % en poids de Y_2O_3 , à la fois dans les états complètement réduits et oxydés, a été étudié à 940° C.

Les solutions solides complètement réduites ne se déforment pas plastiquement sous ces conditions expérimentales, mais des additions d'yttrium à $UO_{2.18-2.20}$ réduisent sa plasticité.

1. Introduction

Previous work has shown that the presence of oxygen in excess of stoichiometry markedly increases the plasticity of uranium dioxide in the temperature range 800° C to 1000° C¹). This extra oxygen is accommodated interstitially in the fluorite lattice. A different type of defect, viz. a defective anionic lattice, is found in the fluorite lattice, when trivalent ions such as Y^{+++} are introduced on cation sites²).

The work to be described was undertaken to determine the effect of such anionic defects on the elevated temperature plasticity of uranium dioxide.

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Le comportement des solutions solides réduites est explicable par l'hypothèse déjà formulée pour expliquer la plasticité améliorée de UO_{2+x} comparée à celle de UO_2 stoechiométrique. Diverses explications du comportement des solutions solides oxydées sont discutées.

Das Kriechverhalten von festen Lösungen aus Yttrium-Oxyd und Uranoxyd in vollständig reduzierten und oxydierten Zuständen wird bei 940° C unter einer maximalen Faserspannung von 5000 psi untersucht. Die festen Lösungen enthielten dabei 0,5 und 1 Gew.-% Y_2O_3 .

Die vollständig reduzierten Lösungen werden nicht plastisch verformt unter diesen experimentellen Umständen. Yttrium-Zusätze zu $UO_{2.18-2.20}$ reduzieren die Plastizität.

Das Betragen der reduzierten Lösungen ist begrenzt erklärbar durch die Hypothese, dass die Plastizität immer besser ist in UO_{2+x} , verglichen mit stöchiometrischem UO_2 . Mögliche Erklärungen für das Betragen der oxydierten festen Lösungen werden diskutiert.

2. Experimental Techniques

2.1. PREPARATION OF UO_2 AND Y_2O_3/UO_2 MIXED CRYSTALS

Preparation of these oxides was undertaken through ammonium diuranate (ADU) as an intermediate.

The method used for the preparation of ADU alone was as follows:

One hundred grams of Springfields oxide was wetted with 60 ml of water and dissolved in 75 ml of nitric acid. The resulting solution was diluted to about 500 ml and filtered on a Buchner filter. The filtrate was made up to

700 ml, heated to 55° C and the excess nitric acid neutralized with 15 ml of ammonium hydroxide. The temperature was adjusted to 60° C and ammonium hydroxide added from a dropping funnel until the solution was alkaline to thymol blue indicator. About 65 ml of ammonium hydroxide was required and was added over a period of 10–15 minutes with constant mechanical stirring. The precipitate was filtered immediately on a Buchner filter and washed with hot water containing a little ammonium hydroxide. Filtration and washing was rapid. The product was dried at 140° C.

When the mixed oxide crystals were needed the method outlined above was modified as follows:

Yttrium nitrate solution containing 40 g Y_2O_3 per litre was prepared by dissolving the BDH hydrated salt in 0.5 *N* nitric acid. Aliquot portions of this solution were added to the uranyl nitrate solution prior to precipitation of the ADU. Additions were made at levels of 0.5 and 1.0 wt % Y_2O_3 in $\text{UO}_2\cdot 6$. These yttrium concentrations are nominal values as the reagent used was not AR quality and is a hygroscopic salt as supplied.

The final precipitate of ADU with or without yttria was decomposed to U_3O_8 by heating in air in a tube furnace for five hours at 700° C. This was then reduced in hydrogen at 700° C for 5 h and the product cooled in argon. The O:U ratios of the powders were varied by controlled oxidation in air at 140° C.

2.2. FABRICATION

To minimise possible complications due to contaminants, no binders were used to aid cold-compacting.

Hydrostatic compacting using a "Vinamould" die within a steel die produced satisfactory green compacts, but in all cases the sintered product had a dense core and porous case. In one specimen containing 1.0 wt % Y_2O_3 , (C 16), measuring approximately 0.9 cm dia. \times 2.5 cm long, the zones were separated by trepanning and checked for any differences in properties. The O:U ratio and yttrium content were found

to be identical in the two zones but the density varied from 9.90 g/cm³ for the outer zone to 10.72 g/cm³ for the inner zone. The two zones were separated by a well defined circumferential crack.

A steel die (0.95 cm wide \times 3.8 cm long, with hemicylindrical ends) was therefore used to press small pieces for creep specimens. Loadings of 4.5 g or 10 g of powder gave sintered pieces that could be cut respectively into two or four test specimens measuring $2.15 \times 0.29 \times 0.18$ cm. Stearic acid in alcohol was used as die lubricant.

Non-stoichiometric specimens were prepared by sintering for 2 h at 1400° C in argon. Stoichiometric sinters were prepared from the non-stoichiometric ones by heating to 1400° C in argon, changing the gas flow to hydrogen, maintaining this atmosphere for one hour and cooling in flowing hydrogen. The hydrogen was purified by passing over heated platinum sponge, anhydrous P_2O_5 : the argon was passed over hot copper foil and P_2O_5 .

The oxygen/uranium ratios for the various specimens were determined by back-oxidation.

2.3. CREEP TESTING

The creep-in-bend test apparatus has been described elsewhere¹). In this present series of tests the temperature was kept constant at 940° C and the maximum fibre stress of the test specimen was maintained at 5000 psi. The furnace atmosphere was purified argon for the non-stoichiometric material and purified hydrogen in the case of stoichiometric samples.

3. Results

After an initial short period all the non-stoichiometric specimens yielded good straight line relationships between deflection and time for periods of up to 400 mins. The results are summarized in table 1.

The deflections observed for the sub-stoichiometric specimens can be accounted for by minor temperature fluctuations, and yttria additions in the fully reduced state would therefore appear to have no beneficial effect upon plasticity, which remains at zero. In contrast yttria

TABLE 1
Properties of urania-yttria solid-solutions

Batch number	Y ₂ O ₃ content (wt %)	Powder properties		Properties of sintered powder					
		Surface area (m ² /g)	O : U ratio	Density (g/cm ³)	O : U ratio	Deflection rate mils†/min			
						Average	Max	Min	
C 19	0.5	6.85	2.28	10.93	2.21	(5)†† 0.050	0.082	0.036	
				10.54	1.997	(3) 0.001	0.003	nil	
C 20	1.0	6.90	2.26	10.85	2.18	(3) 0.047	0.055	0.042	
				10.58	1.99 ₀	(2) nil	nil	nil	
C 21	nil	2.55	2.25	10.93	2.18	(4) 0.135	0.143	0.126	

† 1 mil = 25.4 μ .

†† Number of samples tested.

additions to non-stoichiometric UO₂ appear to inhibit plastic flow.

4. Discussion

The experimental findings that need to be explained are the lack of influence of anionic defects upon the plasticity of UO₂ and the effect of yttria additions in reducing the plasticity of UO_{2+x} at 940° C.

One explanation of the absence of increased plasticity consequent upon the introduction of anionic defects could be that the latter are not present in sufficient numbers. There are no data available on the plasticity of pure UO_{2.01} at the same temperature so comparisons are not possible. However work at the Bettis Laboratories reported by J. Belle ³), has shown that oxygen diffusion in U_{0.9}Y_{0.1}O_{1.98} is considerably faster than in UO_{2+x} and has an activation energy of only \approx 19 kcal/mole compared with 22–32 kcal/mole for UO_{2+x}. Increased anionic mobility associated with the introduction of anionic defects would therefore seem to have no effect upon the plasticity of these solid solutions. In the discussion of the earlier work on the plasticity of UO_{2+x} the conclusion was reached that to explain the experimental observations, irrespective of whether deformation resulted from diffusional creep or from dislocation climb, departure from stoichiometry demanded an increase in diffusion rate of the cation. If this criterion is applied to the case at

present under discussion then the converse should hold, viz. the fact that MO_{1.99} does not deform more readily than MO₂ means that there is no appreciable difference in cation diffusion rates. Again, measurements of uranium diffusion coefficients in U_{0.9}Y_{0.1}O_{1.98} at 1660° C and 1460° C reported by J. Belle ⁴) differ little from those in UO₂. The results of this work therefore support and supplement the findings of the previous work ¹). Measurements of uranium diffusion in UO_{2+x} are however still needed to confirm the hypothesis that the diffusion rate of the slowest diffusing species, viz. the cation, determines the rate of plastic flow of this material.

At the testing temperature, 940° C, the non-stoichiometric specimens all fall close to the UO_{2+y}/UO₂ + U₄O₉ phase-boundary. According to the latest data available ⁵), specimens C 21 (no yttria) and C 20 (1 wt % Y₂O₃) should be single phase, whilst specimen C 19 (0.5 wt % Y₂O₃) should be two phase. High temperature X-ray diffraction patterns of all samples taken at 900° C revealed only a single phase. In the light of this evidence, and the similarity in behaviour of specimens C 19 and C 20, it is believed that an explanation of the difference in behaviour between these specimens and C 21 must first be sought on grounds other than that of difference in amount of second phase present.

Microscopic examination of polished sections of the three samples showed that they were all

two phase, but differed in grain size. The yttria-containing specimens had apparent grain sizes 5 to 10 times greater than the unadulterated uranium oxide. If grain boundary flow contributes appreciably to the overall deformation then an increased grain size in the yttria-containing bodies could explain their increased resistance to deformation. However, it has not been demonstrated that the apparent grain size of the two phase non-stoichiometric oxides at room-temperature is the same as their grain size when single phase at elevated temperature, or indeed that grain boundary flow occurs.

Finally, the yttria might inhibit flow by impeding dislocation movement, either owing solely to the presence of the yttrium ion differing in ionic size from the uranium it replaces, or by adversely influencing the mobility of one or more of the ions present. There is no experimental evidence to support or refute these explanations.

5. Conclusions

Fully reduced solutions of 0.5 and 1.0 wt % Y_2O_3 in UO_2 do not deform plastically at $940^\circ C$. This finding is explicable on the hypo-

thesis, previously advanced to explain the behaviour of UO_{2+x} , that if deformation is diffusion-controlled then it is the diffusion-rate of the slowest diffusing species, viz. the cation, which determines the rate of plastic flow.

Yttria additions to UO_{2+x} reduce its plasticity at $940^\circ C$. There are several possible explanations of this effect and further work is needed to decide the correct explanation.

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