HIGH TEMPERATURE PLASTICITY OF OXIDE NUCLEAR FUEL

by

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Introduction

Because of their importance to both thermal and fast reactor systems the oxide nuclear fuels based on UO_2 are the subject of detailed studies. Of particular technological interest is the plasticity of the fuel inasmuch as it determines the magnitude of fuel swelling and, hence, the stresses induced in the metal cladding (outer fuel container). The amount of permanent deformation allowed in the cladding before the fuel element must be removed from the reactor is limited by both operational and safety considerations. Thus, if less force could be exerted by the fuel on the cladding the useful lifetime of the fuel element could be increased. This realization has been the impetus for several research programs both in the U.S. and in Europe designed to understand the plastic nature of nuclear fuels in a high temperature, fissioning environment. The principle objective is to develop a very plastic fuel that would fill the internal space provided for it without unduly stressing the cladding.

Having established the technological justification for studying the mechanical behavior of oxide nuclear fuels the purpose of this paper is to describe some aspects of the deformation process at high temperatures ($\geq 0.5 T_m$), which also have important implications with respect to the plasticity of non-fissile ceramic oxides. Phenomena associated with low temperature ($< 0.5 T_m$) fission-induced plasticity will be the subject of another paper in this symposium.¹

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It is well known that under certain conditions polycrystalline ceramics deform plastically by mechanisms that involve grain boundaries.²⁻⁴ In fact, it appears that grain boundary sliding (GBS) may enhance the ductility of fine grain ceramics that possess an insufficient number of independent slip systems.⁴ Nevertheless, fracture occurs after relatively low strains since the stress that builds up at discontinuities in the grain boundary (e.g., triple points) cannot be released by slip in the adjoining grains. It follows, therefore, that if sufficient slip systems were available (at modest stresses) in a fine grain ceramic to accommodate the incompatibility due to sliding extensive plasticity (superplasticity?) might be achieved. During the course of our oxide deformation program certain observations have led us to believe that this so-called superplasticity was achieved in both fine grain UO_2 20 wt % PuO_2 materials and larger grain size UO_2 20 wt % PuO_2 containing impurities. These new observations will be described in the present paper and the differences between this and the conventional high temperature deformation behavior of UO_2 ^{5,6} and UO_2 20 wt % PuO_2 ⁶⁻⁹ will be discussed.

Experimental Procedure

The UO_2 -20 wt % PuO_2 specimens were prepared from mechanically blended powders. The fabrication procedure has been reported in detail elsewhere.¹⁰ Tables I and II summarize the principle fabrication variables and sample characteristics and Fig. 1 shows the grain and pore structures of the materials studied.

The specimens were deformed in four point bending in a high temperature, inert atmosphere furnace described in Refs. 10 and 11. Conventional load vs deflection, strain-rate change and stress relaxation tests were conducted

in the strain-rate range of 0.1 to 0.4 h⁻¹ and the temperature range of 1500 to 1800°C.

Results

The deformation behavior of the mixed oxide specimens followed the same general pattern, in that a sharp brittle to ductile transition was observed above 0.5 T_m (the transition temperature increased with increasing strain-rate^{10,11}) and extensive ductility without fracture was recorded only ~100°C above the brittle to ductile transition temperature, Fig. 2. We are concerned here with the plastic regime and the principle deformation parameters are steady state flow stress σ_f and strain-rate sensitivity m .

The analysis of plastic stress and strains in a four point bending test is complex. Heuer, et al⁴ present a treatment of this problem in which m in bending is given by

$$\left(\frac{\partial \ln M}{\partial \ln \dot{\epsilon}} \right)_{\epsilon} \quad (1)$$

where M is the bending moment equal to $\frac{Wa}{2}$ (W = load, and a = distance between inner and outer loading points), and the outer fiber strain-rate is given by

$$\dot{\epsilon} = \frac{12h\dot{\delta}}{3L^2 - 4a^2} \quad (2)$$

where h is the specimen height, $\dot{\delta}$ is the deflection rate of the specimen at its midpoint, and L is the distance between the outer loading points.

The maximum stress in the outer fibers is given by⁴

$$\sigma_{\max} = \frac{Wa}{bh^2} (2 + n + m) \quad (3)$$

where n is the strain hardening coefficient, equal to zero when $\sigma_{\max} = \sigma_f$

$$\text{i.e., } \sigma_f = \frac{Wa}{bh^2} (2 + m) . \quad (4)$$

Thus, the calculated value of σ_f is always less than the value of stress M_R measured from elastic considerations,¹²

$$M_R = \frac{3Wa}{bh^2} . \quad (5)$$

In the following, the flow stress was calculated from load-deflection curves using equations 3 and 4, and the strain rate sensitivity was measured from strain-rate change and stress relaxation tests using Eq. 1. Inasmuch as the σ_f calculation requires knowledge of m we will first describe these results for $\sim 2, 7.6$ and 14.5μ UO_2 20 wt % PuO_2 . The stress-relaxation experiments gave the most reproducible data, and were therefore used to determine m as a function of temperature. Spot checks were made using the strain-rate change test to compute m .

The experimental technique for the stress relaxation experiments is shown in Fig. 3. The stress was allowed to relax from the steady state flow stress at successively lower (or higher) temperatures. As shown in Fig. 4, stress relaxation data were plotted as $\log \partial W / \partial t$ (i.e., load relaxation rate $\equiv \dot{\epsilon}$) versus $\log W$ ($\equiv M$) and the inverse slope of the straight line gave m . The strain rate sensitivity parameter m is plotted as a function of temperature in Fig. 5. The two lines drawn through the data indicate the variation in data points at each temperature and the strong temperature dependence of m . By way of comparison similar data for UO_2 ¹³ is also plotted in Fig. 5.

The flow strength data for UO_2 20 wt % PuO_2 , from equations (4) and (5), are plotted in Fig. 6. The most significant observations are the

strong temperature dependence of the flow strength and the increase in flow strength with increasing grain size. This latter effect is illustrated in Fig. 7 for two temperatures.

The form of the temperature variation of flow stress appears to be exponential. However, a plot of $\log \sigma_f$ vs. $1000/T$ in Fig. 8, indicates an apparent temperature dependence of the activation energy presumably because all the temperature dependent parameters have not been isolated. According to Nicholson this is a common characteristic of superplastic behavior and the correct method of treating the data is not clear.¹⁴

In the majority of tests the specimens were strained to the limits of the extensometer, which corresponded to ~3% outer fiber strain, and then unloaded. However, to demonstrate the unusually high plasticity in these materials, in two tests plastic strain was accumulated by reversing the specimen and bending it back through zero deflection to 3% strain in the opposite direction. In this manner, ~9% strain was accumulated without fracture in a 2 μm grain size specimen and 15% strain was accumulated in a 14.5 μm grain size specimen before slow cracking was observed.

Discussion

The deformation characteristics of these mixed oxide materials compare favorably with those of superplastic alloys.¹⁴ The major points of comparison are (1) strain-rate sensitivities that increase with increasing temperature and lie in the range of 0.4 to 0.8, (2) flow stress is a strong function of temperature, and at high temperatures, decreases to almost vanishingly small values, (3) flow stress increases with increasing grain size over a wide temperature range, and (4) a "temperature dependent" activation energy. In the following, we will discuss these characteristics in relation to observed creep and flow behavior in UO_2 and other UO_2 - PuO_2 materials.

As Fig. 5 shows the strain-rate sensitivities for 15 μm UO_2 in the same stress-strain-rate regime are generally much lower than were observed for the mixed oxide materials and are less sensitive to temperature. The characteristic creep value of $m = 0.22$ (creep exponent = 4.5)^{5,6} appears to be the limiting value at high temperatures. Using these values of m and Eq. it is of interest to compare the temperature dependences of flow stresses calculated from compressive creep data obtained elsewhere⁵ and four point bending data obtained in this program, at a strain rate of $\sim 0.1 \text{ h}^{-1}$. Figure 9 for UO_2 shows quite good comparison between bending and creep flow data, indicating that all UO_2 materials tested behave in a conventional manner. The difference in slopes of the two curves merely reflects slightly different activation energies, which can be explained by small differences in either O/M or in impurity levels in UO_2 .⁶ However, Fig. 10 shows a marked difference between mixed oxide compressive creep data⁷⁻⁹ and the present bending results. The creep data exhibit neither the grain size effect nor the strong temperature dependence of σ_f . The mixed oxides prepared for this program obviously behave in an anomalous fashion, and at this stage, the cause can only be speculated on.

Superplasticity is a characteristic of fine grain materials,¹⁴ and yet in these experiments superplastic characteristics persisted in the 7.6 and 14.5 μm material. In fact, the temperature dependence of m and σ_f for the three grain sizes is remarkably similar and the grain size dependence of σ_f shows no obvious anomaly. If GBS is the dominant mechanism of superplasticity, then it follows that some grain boundary property in the mixed oxides is responsible for retaining the superplastic-like properties beyond the grain size range where they are expected. A preliminary thought is that an iron impurity at the grain boundaries is responsible for this anomalous

behavior, for the following reasons. As Table II shows, the iron content of the two larger grain mixed oxide batches was high, ~1000 ppm. In another part of our mixed oxide deformation and fracture program¹⁰ we had observed a possible trend between ductility and iron content, reproduced in Fig. 11, and in the most impure material that fractured prematurely we observed evidence of a once-liquid phase at the grain boundaries. A tentative explanation for the observed enhanced ductility in these materials could be that a liquid (or near liquid) grain boundary phase facilitates the grain boundary sliding deformation process. Figure 11 indicates that maximum ductility might be achieved with materials containing between 100 and 1000 ppm of iron and possessing between ~2 and 14.5 μm grain size. Other impurities may well contribute the same effect and this would be an interesting area for further study inasmuch as the fissioning process in reactor builds up a significant inventory of insoluble metals in the fuel. Thus, the increased concentration of impurities could perhaps compensate for the increase in grain size caused by the high fuel temperatures, and a high level of plasticity could be maintained throughout burnup.

Summary

Certain UO_2 20 wt % PuO_2 fuel materials fabricated at ANL have demonstrated the possibility of superplastic-like deformation at only 100°C above the brittle-ductile transition temperature. The enhanced ductility, which in one test reached 15% strain in bending, appeared to be facilitated by a grain boundary impurity liquid phase in larger grain size materials.

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TABLE I. Fabrication Variables for UO_2 -20 wt % PuO_2 Specimens

Batch #	Binder	Method of binder addition	Pressing pressure psi	Sintering time & temp. (atmosphere always He-6% H_2)
5	Carbowax 4000	1% binder solution, added to ball-milled slurry before drying	20,000	2 hr at 1625°C
10	Carbowax 4000	1% binder solution, ball milled with powders for 8 hr	20,000	3 hr at 1700°C
11	Carbowax 4000	2% binder solution, ball milled with powders for 8 hr	10,000	Same run as batch 10 (postsinter anneal, 3 hr at 1800°C in He)

TABLE II. Characteristics of UO_2 -20 wt % PuO_2 Batches

Batch #	Immersion density (% TD)	O/M Ratio	Grain Size μm	Impurity content ppm	Fe ppm	Si ppm	Pu Homogeneity (microprobe)
5	96.6 $\pm$.46	1.97 $\pm$.005	$\sim$ 2	400	250	42	Expected ^a single phase
10	96	1.94 $\pm$.005	7.6 $\pm$.4	$\sim$ 1340	970	—	Expected ^a single phase
11	96	1.94 $\pm$.006	14.5 $\pm$ 2.3	$\sim$ 1420	1140	—	Expected ^a single phase

^aApproximately the expected inhomogeneity for mechanically blended material.

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(a) BATCH 5, 96% T.D.
AVERAGE GRAIN SIZE $2\mu\text{m}$

(b) BATCH 10, 96% T.D.
AVERAGE GRAIN SIZE $7.6\mu\text{m}$

(c) BATCH 11, 96% T.D.
AVERAGE GRAIN SIZE $14.5\mu\text{m}$

Fig 2

FIG 3

Fig. 1

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