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Elastic Moduli and Thermal Expansion of
Porous Molybdenum-Uranium Dioxide Cermets

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ELASTIC MODULI AND THERMAL EXPANSION OF POROUS

MOLYBDENUM-URANIUM DIOXIDE CERMETS

by

J. C. Rowley, C. R. Saunders, C. McInteer,

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ABSTRACT

Moduli and thermal-expansion data at high temperature were obtained on a series of sintered molybdenum-uranium oxide cermets as part of an investigation aimed at developing models for predicting the mechanical behavior of porous cermet nuclear fuels. The study indicates that the development of models for predicting the creep behavior and thus the fission-product-induced swelling of these cermets will be extremely complex, and that the development of models for such porous cermets will require an extensive experimental program.

INTRODUCTION AND SUMMARY

Elastic-moduli and thermal-expansion data at high temperatures were obtained on a series of molybdenum-uranium dioxide (Mo-UO₂) cermets.* The cermets were prepared by powder-metallurgy techniques with UO₂ contents of 0, 10, 20, 50, and 60 v/o and with porosities ranging from 3 to 14 v/o. Such cermets, particularly with higher (i.e., ~ 50 v/o) contents of UO₂, are of interest for possible use in fuel elements of thermionic reactors. The data obtained on these well-characterized samples were expected to reveal whether appropriate theoretical models for the mechanical behavior of such cermets can be established. However, the relatively high porosity of the samples makes such model development particularly difficult. The majority of the available theoretical analyses has been restricted to the effects of dilute composite systems, i.e., either to small additions of a second phase to a matrix or to void contents that are small enough to be treated as isolated holes.

The prototype Mo-UO₂ cermets have been specifically fabricated to contain a high proportion of interconnected voids. Such high porosity is desirable because it offers void spaces for fission-gas venting to a significant portion of the UO₂ phase. This venting, however, results in considerable mechanical debonding between the solid phases, and theoretical models for particulate composites with variable bonding between phases have not been formulated. Current analytical formulations predicting mechanical behavior consider individual phase properties, average phase contents, and phase geometries, and always assume continuous-phase boundaries.

It was the primary goal of this study to assess the elastic modulus and thermal expansion of these porous cermets. These relatively simple properties were expected to indicate whether the voids at the interphase boundaries would significantly affect mechanical behavior. The results of these comparisons would then afford a basis for further assessing the more detailed mechanical behavior of such fuels. In particular, if reasonable models

*The notation UO₂ does not imply stoichiometry; the uranium dioxide is in all cases oxygen-rich.

for elastic moduli and thermal expansion could be formulated, it was expected that the creep behavior of such materials could be modeled and their fission-product-induced swelling therefore be predicted.

Excellent high-temperature data for both dynamic elastic modulus and thermal expansion were obtained. However, the elastic-modulus data revealed that the voids at the interphase boundaries strongly affect the mechanical response of these porous cermet, and that the available models therefore are not applicable. The thermal-expansion data could be well represented by a simple volumetric method-of-mixtures theory, and the details of the interphase voids thus are not important. These two contradictory results indicate that the development of theoretical models that will predict the creep behavior and fuel swelling of these cermets will be extremely complex. The creep behavior of these porous Mo-UO₂ cermets will have to be found empirically.

DESCRIPTION AND CHARACTERIZATION OF SPECIMENS

Fabrication

The cermet specimens were supplied as 0.250-in.-diam by 4.5-in.-long rods. The following materials and procedures were used to fabricate these specimens:

- The pure molybdenum specimen was made by loading molybdenum powder (which, as received, had a nominal particle size of 4.8 μ m) into a 9.5-in.-long Plasticol sack of ~ 0.75-in. diam and hydrostatically pressing the powder at 40,000 psi into a rod.
- The specimens containing 10 and 20 v/o UO₂ were made from formulated quantities of nominal 4.8- μ m molybdenum powder blended with nominal 4.5- μ m UO₂.^{*} The pressing procedure was the same as that used for the pure molybdenum rods.
- The specimens containing 50 v/o UO₂ were made from formulated quantities of a nominal 50:50 mixture by weight of 4.8- μ m and 2.0- μ m molybdenum powder that was ball-mill-blended with required amounts of nominal 4.5- μ m UO₂ powder. Because of the higher UO₂ loading, 0.5% paraffin dissolved in

hexane was added to ensure homogeneity of the blend. The pressing procedure remained the same except that a 0.855-in.-diam sack was used.

All above rods were presintered in dry H₂ at 1200°C for 2 h to strengthen them sufficiently for turning to a uniform diameter of 0.35-in. After turning, all pins were given an intermediate sinter of 3 h at 1700°C in dry H₂ plus a final sinter of 6 h at 2000°C in vacuum. After sintering, the rods were centerless-ground to a diameter of 0.25 in. and were then cut to 6.0-in. lengths.

- The 60-v/o UO₂ specimen was made in the same manner as the 50-v/o sample. However, it contained the formulated quantities of nominal 4.0- μ m molybdenum powder which was first blended with 9 v/o of 0.7- μ m tungsten powder. It was then blended with the prescribed quantities of 8.5- μ m UO₂ and was stabilized with 1.5 v/o of < 1.0- μ m Y₂O₃. Paraffin was also added to this blend. The rod was then pressed at 50,000 psi and sintered. Sintering consisted of heating the pressed rod slowly to 500°C in dry H₂ and holding at this temperature overnight. The temperature was raised to 1000°C and held for 0.5 h, after which the temperature was increased to 1700°C where it was held for 3 h. Final sintering consisted of heating to 2350°C for 1 h in argon. The pin received an additional treatment to stabilize the structure by heating to 1900°C for 100 h in argon. All machining was done after final thermal treatment.

Table I summarizes the above starting materials and processes for the cermet samples.

Densities and Porosities

The most important parameter both for evaluating the mechanical properties of the cermet and for assessing the applicability of proposed analytical models is the magnitude and nature of the void. All cermet specimens (except the pure molybdenum rods) were fabricated with ~ 10 to 15 v/o of void. The measured densities of the samples and their calculated void contents are summarized in Table II. Two bulk densities were used in the calculations: (1) those calculated by mass and volume of actual samples, and (2) those measured on

^{*}The uranium in the UO₂ was ²³⁸U.

TABLE I

SUMMARY OF Mo-UO₂ CERMET STARTING MATERIAL AND FABRICATION PROCESSES

Nominal Content, v/o UO ₂	UO ₂ Powder Particle Size, μ m	Mo Powder Particle Size, μ m	Fabrication Processes
0	---	4.8	Hydrostatically pressed at 40,000 psi. Presinter in dry H ₂ at 1200°C for 2 h; intermediate sinter at 1700°C for 3 h in H ₂ ; final sinter at 2000°C for 6 h in vacuum.
10 and 20	4.5	4.8	
50	4.5	50:50 v/o 4.8 and 2.0	
60	8.5 plus 1.5 w/o of < 1.0 Y ₂ O ₃	4.0 plus 9 w/o of 0.7 W	Hydrostatically pressed at 50,000 psi. Slow heat to 500°C in dry H ₂ for 12 h; slow rise to 1000°C, held for 0.5 h; and then raised to 1700°C and held for 3 h. Final sinter at 2350°C for 1 h in argon. Stabilized at 1900°C for 100 h in argon.

TABLE II

DENSITY AND POROSITY CHARACTERIZATION OF Mo-UO₂ CERMETS

Sample No.	Nominal Content, v/o UO ₂	Bulk Density, g/cm ³		Theoretical Density, g/cm ³		Total Calc. void, v/o		Calc. UO ₂ , v/o		Effective Density of Mo Phase, g/cm ³ , and v/o (void of Mo)		Measured Porosities, v/o, and Pore Size Range, μ m
		Calc. ^(a)	Measured ^(b)	Dense UO ₂	97% TD UO ₂	(1)	(2)	(1)	(2)	(1)	(2)	
		(1)	(2)	UO ₂	UO ₂	(1)	(2)	(1)	(2)	(1)	(2)	
5123-1	0	9.860	9.891	10.20	10.20	3.3	3.0	0	0	9.860 (3.3)	9.891 (3.0)	Void: 0.3 open 4.3 closed Size: Not determined
5123-2	10	9.356	9.405 (9.391) ^(c)	10.26	10.24	8.7	8.2	9.1	9.2	9.23 (9.5)	9.28 (9.2)	Void: 9.2 open 1.4 closed Size: 0.12 - 2.0 μ m
5123-3	20	8.989	9.073 (8.923) ^(c)	10.35	10.28	12.6	11.8	17.5	17.6	8.64 (15.3)	8.74 (14.3)	Void: 15.5 open 1.1 closed Size: 0.42 - 2.0 μ m
5123-5	50	8.938	9.087 (8.873) ^(c)	10.59	10.42	14.2	12.8	42.9	43.6	7.66 (24.9)	7.88 (22.6)	Void: 18.8 open 1.1 closed Size: 0.55 - 1.7 μ m
4056X 4057X	60	8.971	9.072 ^(c) (8.890)	10.74 ^(d)	10.55 ^(d)	14.9	14.0	51.1	51.7	7.43 (30.6)	7.61 (28.9)	Void: Not determined Size: Not determined

(a) Calculated from mass and measured volume.

(b) Water immersion data from ~ 1/2-in.-long piece cut from original rods; these data used in elastic modulus-data reduction.

(c) Water immersion data on specimen after test.

(d) Account was taken of the original formulation which contained 9 w/o W in Mo and 1.5 w/o Y₂O₃ in UO₂ powders; Table I.

~ 0.5-in.-long samples cut from the 4.5-in.-long rods, obtained by coating with paraffin and immersing in water.

Because the formulation of the samples was based on component weights and on the desired nominal UO_2 content at theoretical density, the actual amounts of UO_2 were also calculated and are shown in the sixth column of Table II. These quantities are somewhat lower than the nominal quantities. The calculations ensured that the UO_2 particles were at 97% of theoretical density, i.e., were ~ 3% void. The remaining void was arbitrarily taken to be contained in the molybdenum phase, and the seventh column of the table records the resulting net molybdenum "density" and void content. The final column

in Table II records the available data on measured total void and pore size for similar specimens of these cermet. Note that the calculated and measured void volumes are in reasonably good agreement.

The ~ 1% variation in UO_2 content and the ~ 10% variation in calculated void introduced by two different evaluations of the specimen density (Table II) should be remembered in reviewing the subsequent calculations.

Microstructures of Cermets

Photomicrographs of the molybdenum and as-received cermet specimens are shown in Figs. 1 through 5 at magnifications of 100, 250, and 500 for each sample. The white phase is molybdenum, the gray is UO_2 , and the dark areas are void. Figure 5,

Fig. 1. Photomicrographs of as-received molybdenum specimen, ~ 97% of theoretical density.

Fig. 2. Photomicrographs of as-received molybdenum 10-v/o- UO_2 cermet specimens, ~ 8.5 v/o void.

Fig. 3. Photomicrographs of as-received molybdenum 20-v/o- UO_2 cermet specimens, - 12.2 v/o void.

Fig. 4. Photomicrographs of as-received molybdenum 50-v/o- UO_2 cermet specimens, - 13.5 v/o void.

Fig. 5. Photomicrographs of as-received molybdenum 60-v/o- UO_2 cermet specimens, - 14.5 v/o void.

which presents photomicrographs of the 60-v/o- UO_2 cermet, indicates that:

- The void distribution is very complex for cermets with higher contents of UO_2 .
- The voids are obviously not spherical, and there is a rather wide range of pore sizes.
- It is only a matter of convenience in visualization and simplification of the analysis to treat the void as associated with either the molybdenum or the uranium-dioxide phase.

The structure of the cermet at the higher contents of UO_2 could be described as a sponge of molybdenum with interconnected porosity into which UO_2 particles have been dispersed. Note for subsequent discussions that, generally, neither the molybdenum phase nor the UO_2 phase completely surrounds the other. This observation is important in the interpretation of the data obtained.

Electrical Resistivities

The electrical resistivities of the specimens were measured precisely after the moduli had been determined. The data are recorded in Table III. As a first step in studying the void content calculated for the molybdenum phase, a simple analytical model for the electrical resistivity of the porous samples was evaluated. The analytical representation of electrical resistance is far simpler than mechanical modeling and should result in reasonably accurate predictions. The model of Kerner,¹ is used, which assumes that the void is present as uniformly spaced spheres of uniform size. Thus,

$$\frac{R}{R_0} = (1 + V_t/2)/(1 - V_t) \quad (1)$$

where V_t is the total volume fraction of insulating constituents (as uniform spheres) and R_0 is the resistivity at theoretical density. Because the electrical resistivity of UO_2 is $\sim 10^4$ to $10^5 \Omega/\text{cm}$ (10^{10} to $10^{11} \mu\Omega/\text{cm}^2$) and the resistivity of molybdenum at 25°C and theoretical density³ is $R_0 = 5.78 \mu\Omega/\text{cm}$ (at 27°C), the UO_2 can be considered as an insulator and its amount (v/o) can be added to that of the void. Therefore,

$$V_t = v/o \text{ UO}_2 + v/o \text{ Void} = V_{\text{UO}_2} + V_{\text{void}}$$

Figure 6 is a plot of the resistivity data in Table III compared to the simple theoretical predictions of Eq. (1).

The agreement between the data and Kerner's model for pure molybdenum and 10-v/o UO_2 cermet is very reasonable. Figures 1 and 2 reveal that these two materials might reasonably be expected to behave as assumed by the theoretical model. From the data trend shown, already at 20 v/o UO_2 the cermet is of higher resistance than calculated; and Fig. 3 indicates that the void structure and UO_2 particles are far from the simple uniform-sphere model. Figure 6 also shows that the 50- and 60-v/o UO_2 cermets have resistances that are considerably higher than the theoretical values, but, as indicated, the volume content of UO_2 plus void exceeds the theoretical limit of applicability of the model. A study of the photomicrographs in Figs. 4 and 5 for the 50- and 60-v/o- UO_2 cermets shows clearly that their structure is only a pseudocontinuous molybdenum phase. The resistivity data, although higher than predicted by the model, do indicate that the molybdenum phase,

TABLE III
ELECTRICAL RESISTIVITIES OF Mo- UO_2 CERMET SAMPLES AT 25°C

Sample No.	UO_2 Content, v/o		$V_t^{(a)} = V_{\text{UO}_2} + V_{\text{void}}$	Measured Specific Electrical Resistivity, $\mu\Omega/\text{cm}$
	Nominal	Calculated ^(a)		
5123-1	0	0	3.3 - 3.0	5.91
5123-2	10	9.1 - 9.2	17.8 - 17.4	7.89
5123-3	20	17.5 - 17.6	30.1 - 29.4	11.63
5123-5	50	42.9 - 43.6	57.1 - 56.4	22.47
4056X	60	51.1 - 51.7	66.0 - 65.7	69.63
4057X				

(a) Range in calculated values results from variations in results of density determinations; see Table II.

Fig. 6. Room-temperature electrical resistivity of Mo-UO₂ cermet, vs volume percent void plus nonconducting UO₂ phase. Comparison with theoretical model.

even though somewhat discontinuous, does dominate the electrical conduction properties of the cermet.

The evidence thus far indicates that some difficulties will be encountered in attempting to propound theoretical models for predicting the mechanical behavior of cermets with higher UO₂ content.

Spectrographic Impurities

The ~ 0.5-in.-long rod samples were submitted to spectrographic examination, which indicated a high degree of purity for the as-received samples. Table IV records the major impurities and lists all those that were spectrographically detected to amount to at least 100 ppm.

The 60-v/o-UO₂ cermet contained yttrium and tungsten which, however, had already been present as additives in the original formulation.

TABLE IV
SUMMARY OF SPECTROGRAPHIC IMPURITY DETERMINATION

Nominal Sample Composition	Major Impurities Detected, ppm
Mo	< 100
Mo - 10 v/o UO ₂	Fe, 100 ^(a)
Mo - 20 v/o UO ₂	Fe, 200 ^(a)
Mo - 50 v/o UO ₂	Fe, 300 ^(a) Al, 100 ^(a) Cr, 100 ^(a)
Mo - 60 v/o UO ₂	Al, 200 ^(a) Fe, 100 ^(a)

(a) Based upon the specimen as MoO₃-U₃O₈; impurities < 100 ppm not reported.

X-Ray Diffraction and Chemical Analysis Results

Samples of both the as-received and tested* cermets were submitted to x-ray diffraction and chemical analyses. The results indicated that the nominal 10- and 20-v/o-UO₂ cermets essentially retained their initial structure up to 1350°C when exposed to the modulus and thermal-expansion environment of the test apparatus, i.e., to carbon and a slight overpressure of high-purity argon. However, the molybdenum in the nominal 50- and 60-v/o-UO₂ cermets exposed to temperature slightly above 1600°C did react with carbon. Because the reaction probably had not proceeded very far at 1500°C; the data up to this temperature are assumed to be unaffected.

The x-ray diffractometer surface scans taken after testing yielded the results shown in Table V.

The results of pretest chemical analysis for the 10-, 20-, and 50-v/o-UO₂ composites are shown in Table VI. The O/U molar ratio in all cases is approximately two and shows that the uranium oxide was near, but probably slightly above, stoichiometric composition.

The results of posttest chemical analysis on the nominally 60-v/o-UO₂ specimen showed 51.2 v/o U, 36.4 w/o Mo, 3.08 w/o W, 1.03 w/o Y, and 1.01 w/o total C. Oxygen by difference is 7.28 v/o. Probably all carbon is combined as Mo₂C and in solid solution with b.c.c. molybdenum. The carbon in these posttest samples came from the graphite heater during the high-temperature modulus and thermal-expansion runs.

*After modulus and thermal-expansion data had been obtained in a furnace with graphite heater and -1 atm of pure argon.

TABLE V
POSTTEST X-RAY DIFFRACTOMETER RESULTS
(Surface Scans)

Nominal Sample Composition	Maximum Test Temperature, °C (a)	Phases Found
Mo	1338	b.c.c. phase with $a = 3.147 \text{ \AA}$
Mo-10 v/o UO_2	1335	b.c.c. phase with $a = 3.147 \text{ \AA}$ f.c.c. UO_2
Mo-20 v/o UO_2	1638	b.c.c. phase with $a = 3.147 \text{ \AA}$ f.c.c. UO_2 ; orthorhombic $\text{Mo}_2\text{C}(b)$
Mo-50 v/o UO_2	1641	b.c.c. phase with $a = 3.147 \text{ \AA}$ f.c.c. UO_2 ; orthorhombic $\text{Mo}_2\text{C}(b)$
Mo-60 v/o (c) UO_2	1628	b.c.c. phase with $a = 3.147 \text{ \AA}$ f.c.c. UO_2 ; orthorhombic $\text{Mo}_2\text{C}(b)$

(a) Maximum temperature of modulus and thermal-expansion runs.

(b) Pseudo-hexagonal.

(c) The tungsten and Y_2O_3 in the starting material are probably present in solid solution in the phases found.

TABLE VI
CHEMICAL ANALYSIS RESULTS FOR Mo- UO_2 CERMETS

Nominal Cermet Composition	Content, v/o		Oxygen by Difference, v/o
	U	Mo	
Mo-10 UO_2	9.10	90.0	0.9
Mo-20 UO_2	18.3	79.1	2.6
Mo-50 UO_2	36.7	58.4	4.9

STABILITY OF SPECIMENS

The specimen dimension and weight changes as determined from pre- and posttest measurements on the modulus-thermal expansion samples are summarized in Table VII. The largest changes are the ~ 1% mass losses noted for the cermet samples containing 20, 50, and 60 v/o UO_2 . These large values were caused by exposure to higher temperatures and by carbiding which occurred at the last few data hold points above ~ 1500°C.

TABLE VII
PERCENTAGE CHANGES OF Mo- UO_2 SPECIMEN DIMENSIONS AND MASSES DURING MODULUS AND THERMAL EXPANSION DETERMINATIONS

Sample No.	Nominal UO_2 Cont., v/o	Length Change, %	Diam. Change, %	Weight Mass Change, %	Max. Test Temp., °C
5123-1	0	+ 0.025	+ 0.200	+ 0.001	1338
5123-2	10	+ 0.020	- 0.14	- 0.028	1335
5123-3	20	+ 0.046	- 0.040	- 1.09	1638
5123-5	50	+ 0.035	- 0.020	- 1.18	1641
4056X 4057X	60	+ 0.045	0.060	- 0.52	1628

(a) Original specimens were nominally 0.250-in.-diam by 4-in.-long rods, with nominal weights of from 31.5 to 28.0 g.

DYNAMIC ELASTIC MODULI AND THERMAL EXPANSION DATA

Experimental Method

The experimental apparatus was an adaptation of that described by Brown and Armstrong.⁴ Briefly, this apparatus is a high-temperature furnace equipped with graphite heater elements and graphite radiation shields that can be routinely used to 2500°C, with 2700°C as the upper limit of operation. A slight overpressure, ~ 1 psi, of pure dry argon is used as atmosphere for high-temperature property determinations.

The dynamic modulus, Young's modulus, and shear modulus were obtained by the longitudinal and rotational resonant vibrations of a centrally supported, ~ 4-in.-long by 0.250-in.-diam thin rod sample. The thermal expansion was determined by two precision filar eyepiece microscopes viewing the sample ends through optical ports in the body of the high-temperature furnace. The thermal-expansion data were used in reducing the moduli to adjust the bulk density and length changes to their correct values at elevated temperatures.

Data Summary

Table VIII summarizes the room-temperature moduli and thermal-expansion data obtained. Also included are results for two materials frequently used in the fabrication of thermionic-converter fuel pins: tungsten and TZM alloy.

The molybdenum Young's modulus of 43.71×10^6 lb/in.² (~ 3 v/o porosity) compares very favorably with literature values;⁵ e.g., 47.48×10^6 (25°C)

TABLE VIII
SUMMARY OF MODULI AND THERMAL EXPANSION DATA, Mo AND Mo-UO₂ CERMENTS -
COMPARISON WITH TUNGSTEN AND TZM ALLOY

Sample Identification	U ₃ Content, v/o		Sample Bulk Density, g/cm ³	Av Total Void, v/o	Room Temperature Elastic Moduli, lb/in ² x 10 ⁶				Mean Coefficient of Thermal Expansion (α), 10 ⁻⁶ /°C			Comments
	Nominal	Av Calc.			Young's Modulus (E) (%)	Shear Modulus (G) (%)	Bulk Modulus (K) (%)	Poisson's Ratio (ν) (%)	20-500°C	20-1000°C	20-1500°C	
5123-1	0	0	9.891	3.2	43.71 ^(a) (30.73)	16.93	34.84	0.291	5.70	5.95	—	Max. temp. 1338°C
5123-2	10	9.2	9.405	8.5	35.90 (24.76)	14.05	26.90	0.278	5.92	6.32	—	Max. temp. 1335°C
5123-3	20	18	9.073	12.2	29.00 (20.00)	11.48	20.40	0.263	6.44	6.77	7.42	Max. temp. 1638°C
5123-5	50	43	9.087	13.5	23.54 (16.23)	9.43	15.58	0.248	7.04	7.47	8.23	Max. temp. 1641°C
4056X 4057X	60	52	9.072	14.5	20.69 (14.26)	8.13	15.15	0.272	7.58	8.37	9.47	Max. temp. 1648°C
Tungsten AGARD	0	0	19.25	—	59.47	23.20	45.40	0.282	4.79	4.90	5.17	Included for com- parison
TZM LASL	0	0	19.17	—	48.17	17.56	62.92	0.372	5.76	6.05	—	Included for com- parison Max. temp. 1377°C

(a) Units of 1000 kg./cm².

for a dense sample of molybdenum and 59.33×10^6 at room temperature for tungsten as compared to a LASL value of 59.47×10^6 lb/in².⁵

Temperature Dependence of Properties

The temperature dependence of the dynamic elastic moduli is shown in Figs. 7 through 10. The consistency of the data is evident, and the general agreement in shape of the Young's modulus and shear modulus curves for the cermets of the same UO₂ content is clearly indicated.

Figures 8 and 10 are plots of the respective ratios of reduced moduli, at elevated temperature

vs room-temperature values. These curves accentuate the expected similarity of the temperature-dependence of the two moduli. They also illustrate that for the 20-v/o and higher-v/o-UO₂ cermets, the two phases are interacting differently as the temperature is raised and approaches the sintering temperature of ~ 2000°C. This general type of mechanical behavior has been noted for several other particulate composites systems.

The thermal-expansion data as a function of temperature are plotted in Fig. 11. Figure 12 records the mean coefficients of thermal expansion

Fig. 7. Temperature dependence of Young's modulus of Mo-UO₂ cermets.

Fig. 8. Temperature dependence of reduced Young's modulus, Mo-UO₂ cermets.

Fig. 9. Temperature dependence of shear modulus for Mo-UO₂ cermets.

Fig. 11. Thermal expansion of Mo-UO₂ cermets (20° to t°C).

Fig. 10. Temperature dependence of reduced shear modulus for Mo-UO₂ cermets.

Fig. 12. Mean coefficient of thermal expansion for Mo-UO₂ cermets.

derived from the data in Fig. 11, in the form

$$\bar{\alpha} = \frac{\Delta L}{L_{20} (t - 20)}.$$

The thermal expansion of the cermets is seen to increase progressively with UO₂ content, which is generally as expected, because UO₂ has a higher expansivity than molybdenum.

ANALYSIS OF DATA AND DISCUSSION

General

This study had been designed to explore the applicability of theoretical models to the mechanical

behavior of Mo-UO₂ cermets. Although uranium-oxide contents ranging from 40 to 60 v/o are of highest practical interest for nuclear fuels, other variations in composition and porosity are also needed to assess the applicability of such models. In addition, the properties of the two phases (in this case, molybdenum and UO₂) as they occur in the as-fabricated composite body must be known, and the effects of voids or porosity in the cermets must be evaluated. These latter effects were not obtained directly because only one specimen had been prepared for each void content. The needed data were therefore obtained from published results of other

reliable investigations of similar materials, and the work of Claussen was heavily drawn upon.⁶ The properties of UO_2 were also obtained from the literature.

Estimated Stresses and Differential Shrinkages During Cooldown

Of particular significance for these estimates is the very large difference in thermal expansion between the two phases of the cermet. Available data clearly indicate a linear expansion (or contraction) difference of about,

$$\Delta\alpha \approx 4 \times 10^{-6}/^{\circ}\text{C}$$

between UO_2 and molybdenum. During cooldown from the sintering temperature ($\sim 2200^{\circ}\text{C}$) to ambient, large stresses may therefore develop within the cermet and, if the interfaces of the phases separate, voids will be created.

The magnitudes of the interparticle stresses can be roughly estimated by using the simple relation,

$$\sigma_r = \frac{(T_s - T)(\alpha_m - \alpha_i)}{\left[\frac{(1+\nu_m)}{2E_m} + \frac{(1-2\nu_i)}{E_i} \right]}$$

where:

σ_r = radial interface stress,

T_s = sintering temperature (or a temperature level at which both constituents have some rigidity),

T = temperature of interest, below the sintering temperature, and

m, i = matrix and inclusion property, respectively.

This estimating formula assumes that the two phases are perfectly bonded at the interfaces of the particles. For the purposes of this rough estimate, take the following nominal values.

UO_2	Molybdenum
$\nu \approx 0.3$	$\nu \approx 0.3$
$E \approx 0.9 E_0 = 29.2$ $\times 10^6 \text{ lb/in.}^2$	$E \approx 0.7 E_0 = 30.6$ $\times 10^6 \text{ lb/in.}^2$
$\alpha \approx 11.0 \times 10^{-6}/^{\circ}\text{C}$	$\alpha \approx 7.0 \times 10^{-6}/^{\circ}\text{C}$

Table IX records the results of these cooldown-interaction stress calculations for two different models: a molybdenum matrix and a uranium-oxide matrix. Figure 13 illustrates the two situations, the directions of the stress components, and their probable consequences.

TABLE IX
ESTIMATES OF COOLDOWN STRESSES
IN A $Mb-UO_2$ CERMET

Temperature Decrease, $\Delta T = (T_s - T),$ $^{\circ}\text{C}$	Stress Component (a)	Estimated Magnitudes of Cooldown Stresses, ^(b) lb/in. ²	
		Molybdenum Matrix	Uranium Oxide Matrix
1500 (Cooldown to ambient temperature)	σ_r	+190,000	- 162,000
	σ_t	- 95,000	+81,000
100 (A sensitivity estimate)	σ_r	+12,700	- 10,800
	σ_t	+ 6,400	- 5,400

(a) σ_r is the radial stress component at the $Mb-UO_2$ interface, σ_t is the tangential stress component in the matrix; see Fig. 13.

(b) Positive values denote tension, negative compression.

Fig. 13. Illustration of cooldown stress, cracks, and void due to cooldown from fabrication temperature of $Mb-UO_2$ cermet.

As a point of reference for comparing the magnitudes of these stress results, the modulus of rupture for bulk UO_2 is reported to be ~ 84 to 180 MPa ($12,000$ to $26,000$ $lb/in.^2$).^{7,8}

If the phases are strongly interacting mechanically, this simple stress calculation indicates that:

- The UO_2 particles will crack at ambient temperatures after fabrication.
- For a cermet with the molybdenum matrix predominating, there may be some interface separation of the UO_2 inclusions from the molybdenum matrix.
- In either event, theoretical-model calculations which start with the measured moduli of the pure constituents will yield too high values for the modulus of the cermet.
- This type of UO_2 cracking could be very beneficial for the fission-gas release from the UO_2 particles.

Note that even as small a temperature change as $100^\circ C$ generates very large interaction stresses, principally because of the large difference in thermal expansion of the two phases. Also, the UO_2 particles become ductile at elevated temperature, i.e., at $\sim 1400^\circ C$ according to Evans and Davidge.⁸

The phase character for these cermets, as illustrated in Figs. 2 through 5 (except possibly at the 10- and 20-v/o- UO_2 levels) resembles neither of the two extremes shown. For the two low- UO_2 cermets (see Figs. 2 and 3), the stresses calculated for the predominating molybdenum matrix could be reasonable.

Because the case of a predominating molybdenum matrix is of greatest interest for present applications, the stress estimates indicate that some interaction void is probably generated between the UO_2 phase and the molybdenum in the Mo- UO_2 cermet as the cermet cools down. The upper bound to this differential shrinkage volume can be estimated simply by considering the UO_2 particles to be completely loose (i.e., not bonded to the molybdenum). Then the volume-fraction void, based upon the total volume of the cermet, can be estimated by the approximation:

$$\frac{\Delta V}{V} \approx 3\alpha \Delta T V_{UO_2},$$

where V_{UO_2} is the volume fraction of UO_2 in the cermet. This is a calculation for the differential volumetric shrinkage of the "holes" occupied by the UO_2 particles in the molybdenum matrix. For the parameters assumed above, the relative interaction void is less than

$$\frac{\Delta V}{V} \text{ interaction void} \leq 1.8 \times 10^{-2} V_{UO_2},$$

or the differential shrinkage void can be expected to be less than $\sim 2\%$. Although the differential shrinkage will not generate large voids, note that some decrease in the effective rigidity of the UO_2 phase can be expected due to cracking of the UO_2 , to some debonding at the Mo- UO_2 interfaces, or to a combination of both phenomena.

Modulus-Porosity Relations

The evaluation of the modulus values determined in this study requires that the data be referred to a common base. The most convenient approach is to correct to the expected values at theoretical density. Note that the derived correlations of porosity dependence of moduli do not account for the portions of the surfaces at the interfaces between particles that are not bonded.

Claussen⁶ determined that the relation of Young's modulus, E , versus porosity, p , for powder-metallurgically fabricated molybdenum^{*} is given by,

$$E = 31.8 \times 10^3 (1 - 2.0 p) \text{ (kgf/mm}^2\text{)} \\ = 45.2 \times 10^6 (1 - 2.0 p) \text{ (lb/in.}^2\text{)},$$

which indicates that the present molybdenum sample at $p = 0.033$ to 0.030 should have modulus values of

$$E = 42.5 \text{ to } 42.2 \times 10^6 \text{ lb/in.}^2,$$

which obviously compares favorably with the value of 43.71×10^6 $lb/in.^2$ measured on the molybdenum sample (see Table VIII).

The porosity-modulus relations obtained by Claussen are reproduced in Fig. 14, with the present room-temperature data (converted to units of kgf/mm^2) of this study for the molybdenum and 52-v/o- UO_2 specimens plotted for comparison. Evidently, these porosity correction relations can be applied with reasonable confidence to the Mo- UO_2 cermet

* Claussen's specimens were vacuum hot-pressed for 15 min at $1500^\circ C$ with 400 kgf/cm^2 (5800 $lb/in.^2$) from $1.5\text{-}\mu m$ molybdenum powder.

Fig. 14. Influence of porosity on modulus of Mo, UO_2 , and a 52-v/o- UO_2 Mo- UO_2 cermet. (Plot is adapted from Fig. 2 of Ref. 6; data from this study.)

samples of this study. This is particularly rewarding because Claussen used a different method of determining modulus, i.e., strain-gauging with mechanical loading to obtain data on pressed disks. It is also remarkable that a linear relation between porosity and modulus was obtained for the wide range of void content (> 20 v/o) studied.

The modulus-porosity relation derived for the Mo- UO_2 cermet is then given as,

$$E_{TD} = \frac{E}{1 - [3.1f_{UO_2} P_{UO_2} + 2.0f_{Mo} P_{Mo} + 3.0P_1]} \quad (2)$$

where:

E = measured modulus,

E_{TD} = modulus at theoretical density,

f = volume fraction of the component,

P_{UO_2} = volume-fraction porosity in UO_2 phase,

P_{Mo} = volume-fraction porosity in Mo phase, and,

P_1 = volume-fraction porosity associated with the phase boundaries

$$= P_{total} - (f_{UO_2} P_{UO_2} + f_{Mo} P_{Mo})$$

From photomicrographs (e.g., Figs. 2 through 5) it is evidently difficult to systematically assign a specific amount of the void to each phase and to decide which portion of the porosity is to be considered as being at the interphase boundaries. Also, recall that when the porosity is removed (analytically) from the specimens the actually determined UO_2 content approaches the nominal values, because the original weight formulations of the cermet were for the nominal contents of UO_2 .

Physically, Eq. (2) gives a relation for estimating the reduction factor from the theoretically dense value if the distribution of the void between the UO_2 , molybdenum, and the phase interfaces can be assessed. The factor is rather sensitive to the assumption of allocated void distribution. Table X records the calculated porosity-modulus reduction factors for six different assumptions: (1) all void in the molybdenum, (2) all void in the UO_2 , (3) all void associated with the interfaces, (4) the suggestion of Ref. 6, (5) the simple relation $E = E_0(1-2.6p_t)$, and, finally, (6) an adaptation of Claussen's results with the factor for interphase void reduced to 2.5 from 3.0 (Eq. 3).

TABLE X
COMPARISON OF POROSITY-MODULUS REDUCTION FACTORS

Nominal Cont., v/o UO_2	Av Calc. v/o UO_2	Av Total Void, v/o	Porosity-Modulus Reduction Factors for Various Assumptions					Claussen's Approach, With P_1 Factor 2.5, Eq. (2)
			All Void in Mo Phase	All Void in UO_2 Phase	All Void in Inter- phase	Claussen's Relation at 55 v/o UO_2 (1-2.6 P_t)	Claussen's Approach $P_{UO_2} = 0.03$, $P_{Mo} = 0.032$ Using Eq. (1)	
0	0	3.2	0.936	--	--	--	--	--
10	9.15	8.45	0.846	0.976	0.747	0.782	0.773	0.800
20	17.5	12.2	0.798	0.934	0.634	0.683	0.626	0.703
30	43.3	13.5	0.848	0.819	0.995	0.649	0.608	0.662
60	51.5	14.5	0.899	0.768	0.965	0.623	0.574	0.634

In Claussen's work, the cermet was determined to have ~ 8.5 v/o void. The molybdenum phase was determined from the pure molybdenum rod to have ~ 3.2 v/o, and the UO_2 was estimated to have a void of ~ 3.0 v/o. Thus, the cermets of Ref. 6 had only 1 to 2 v/o interphase void, whereas the specimens used in this study had ~ 10 v/o interparticle void content, and therefore, the factor of 3.0 in Eq. (2) becomes of dominating influence. The calculated porosity-reduction factors in the first five columns of Table X give poor representations of the modulus at theoretical density. Exploratory calculations indicated that the reduction factor resulting from the empirical value of 3.0, applied to the interphase void, is too strong and that this value should be closer to ~ 2.5. The modulus-porosity reduction relation is then,

$$E_{TD} = \frac{E}{1 - \left[3.1f_{UO_2} P_{UO_2} + 2.0f_{Mo} P_{Mo} + 2.5P_1 \right]}, \quad (3)$$

where only the factor 2.5 applied to the interphase void, P_1 , is changed from Eq. (2).

Figure 15 shows the room-temperature elastic-modulus data (Table VIII), values extrapolated by Eq. (3), and a comparison with Claussen's results all plotted vs v/o UO_2 . (The figure is adapted from Fig. 3 of Ref. 6.) This plot shows that the Mo- UO_2 cermets of this study have a rather close relation to those prepared by Claussen. Also shown on the figure are the theoretical bounding models which assume continuous interfaces between the molybdenum and UO_2 particles. It is very evident that the data for these cermets (as well as those of Ref. 6) do not follow the bounding trends of the theoretical model when the phases are assumed to be continuously bonded. This divergence is expected, because the Mo- UO_2 cermets, as-fabricated with significant void contents (shown clearly by their microstructures), have substantial portions of their interphase boundaries disconnected, which was the major objective of the fabrication procedures. The difference between the theoretical results of the continuous-phase model and the values extrapolated to theoretical density is a qualitative estimate of the degree to which the phase boundaries are not bonded. This result is also a quantitative confirmation that the desired void structure has been achieved: the UO_2 particles are in communication with the void and

Fig. 15. Young's modulus of Mo- UO_2 vs v/o UO_2 phase. Corrections for porosity obtained by the method of Claussen. Curves adapted from Fig. 3 of Ref. 6.

thus will allow escape of some portion of the fission gas. Also, the nonbondedness of the interphase boundaries will allow considerable fission-induced swelling of the UO_2 with a relatively weak mechanical interaction with the molybdenum matrix.

The theoretical bounding models depicted in Fig. 16 are based essentially on a "parallel" uniform-strain model and on a "series" uniform-stress model; both with complete continuity and bonding of the interfaces of the phases. Figure 16 shows schematically this ideal model contrasted with a simplified sketch of the actual situation. This sketch also points out the need for considerably more parameters to describe the true mechanical character of the phase interactions in addition to accounting for the amount of void at the phase boundaries.

Temperature Dependence of Cermet Moduli

The above discussion clearly points out that attempts to account quantitatively for the temperature dependence of the cermet elastic moduli, Figs. 7 through 10, will fail without an appropriate model.

Fig. 16. Schematic illustration of interphase void effect on mechanical behavior of Mo-UO₂ ceramets. Upper and lower bound models for modulus prediction, per Fig. 15.

Fig. 17. Temperature dependence comparison of the elastic modulus of Mo and UO₂. Note lower rate of softening.

Figure 17 compares the temperature-dependence of the two phases, molybdenum and UO₂, and indicates that the UO₂ modulus will decrease less rapidly than the

modulus of the molybdenum; thus, the trend of decreasing slope with temperature for increasing UO₂ content in Fig. 7 is as expected. The detailed shape of the curves is probably a result of the changing interaction between the two phases as the UO₂ particles expand more with increasing temperature than the molybdenum phase.

Thermal Expansion

The magnitudes of thermal expansion of the ceramets plotted in Figs. 11 and 12 increase with UO₂ content, but the detailed shapes of the temperature dependence are also affected by the mechanical interactions of the two phases. Because this interaction is changing with temperature, as discussed above, it is not possible to quantitatively model these materials. The theoretical approaches to date rely on the full bond at the interfaces of the phases (see, for example, Ref. 10).

The thermal-expansion trends with UO₂ content are shown in Fig. 18, and the thermal-expansion characterization of the two phases is recorded in Fig. 19.

Fig. 18. Mean coefficients of thermal expansion for Mo-UO₂ ceramets vs UO₂ content, indicating essentially linear (method of mixtures) dependence.

Fig. 19. Comparison of mean thermal-expansion coefficients of molybdenum and UO_2 (from 20° to t°C).

It is obvious from Fig. 19 that the simple method-of-mixtures model represents the data fairly well,

$$\bar{\alpha}_c \approx V_{\text{UO}_2} \bar{\alpha}_{\text{UO}_2} + V_{\text{Mo}} \bar{\alpha}_{\text{Mo}},$$

as indicated by the straight lines plotted in the figure. The data for nominal 50-v/o UO_2 cermet seem somewhat anomalous. The thermal-expansion behavior noted is quite similar to that observed by Tummala and Friedberg for tin-zirconia and tin-silica cermets.¹¹

CONCLUSIONS

Modulus and thermal-expansion data at high temperature were obtained on a series of sintered Mo- UO_2 cermets. Analyses of the data show that the specimens represented a consistent system from pure molybdenum to 60-v/o- UO_2 cermet. The desired high void contents, ~ 10 to 15 v/o, that were achieved, affect the modulus data significantly, but not the thermal-expansion behavior.

Specifically:

- Theoretical models of the moduli characteristics are not available due to the large effect of the interphase voids.
- Empirical linear relations in porosity content for reduction of the moduli data to

values of theoretical density are available, and the data follow rather closely those reported previously for similar cermets.

- The thermal-expansion results indicate that the cermets closely follow the simple-mixture model, and are affected insignificantly by porosity.
- Photomicrographs confirm the presence of significant interphase void in the structure of the cermets, with the sintered particles of the two phases near theoretical density.
- The samples were very stable in the high-temperature runs (in argon), except when the graphite furnace exceeded ~ 1500°C and some of the molybdenum phase carbided.

The study indicates that the development of models which might predict the creep behavior and fuel swelling of these cermets will be extremely complex because of the strong effect of the desirable interphase porosity. The creep behavior of these porous cermets will have to be found empirically in an experimental program.

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