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PREPARATION AND PROPERTIES OF UO_2 CERMET FUELS

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PREPARATION AND PROPERTIES OF UO_2 CERMET FUELS

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Sintering, hot-press forging, and gas-pressure bonding were evaluated as techniques for preparing cermet fuel materials containing at least 60 volume per cent UO_2 and having a minimum density of 90 per cent of theoretical. Minus 325-mesh chromium, molybdenum, niobium, and Type 302B stainless steel were employed as matrix materials. Hydrothermal and spherical UO_2 powders were evaluated.

Cermets containing 80 volume per cent UO_2 and exhibiting densities in excess of 90 per cent of theoretical were successfully prepared by both hot-press forging and by gas-pressure bonding mixed oxide and metal powders. Gas-pressure bonding produced specimens with a more uniform structure and was demonstrated to be capable of simultaneously densifying and cladding green-pressed cermet fuels. Spherical UO_2 powders produced the more homogeneous microstructures. Excellent microstructures were also obtained by the use of UO_2 powder coated with niobium by vapor-deposition techniques.

So far as direct comparison is possible the cermets were superior in strength to UO_2 . Strength, which was measured by bend and compression tests, was density dependent. Thermal-conductivity values for the cermets were far higher than values for UO_2 .

Electrical-resistivity data were also obtained. These data were used to develop a mathematical correlation of electrical and thermal conductivity but a complete analysis could not be made on the basis of present theories due to the limited number of measurements made.

INTRODUCTION

Bulk UO_2 is perhaps the most acceptable fuel for power reactors today, and its use for this application will no doubt continue to increase during the forthcoming years. However, the thermal and mechanical properties of UO_2 do place certain restrictions on the utilization of this material. The poor thermal conductivity of UO_2 limits both the size and the operating temperature of solid UO_2 elements in order to avoid central melting. Improvements in the mechanical properties of UO_2 could raise the burnup capability of the fuel by providing better resistance to stresses which fracture UO_2 during irradiation. Lower fuel temperatures resulting from improved thermal conductivity should also increase the gas-retention capabilities of the fuel.

Perhaps still another limitation of solid UO_2 fuel is that in high-temperature applications where the structural integrity provided by the thin metallic cladding is marginal, the presence of the UO_2 adds little or no strength unless of course the destructive stresses are predominantly compressive.

It, therefore, seemed worthwhile to determine what improvements might be obtained in both the physical and mechanical properties of UO_2 by the addition of a moderate amount of metal. The presence of the metal, if it is continuous throughout the structure, should also provide over-all structural integrity by bonding to the cladding at the

interface. It was recognized that improved properties would not necessarily provide a superior fuel if the fabrication processes were unduly complicated and, hence, expensive. This latter point provides some guidance throughout the studies.

Potential methods for securing better properties in UO_2 -base fuels have been under investigation for a number of years. Some improvements in thermal and mechanical properties have been obtained by the addition of impurities or metal fibres to UO_2 and other ceramics.⁽¹⁻³⁾ Dispersion fuels with UO_2 have received extensive study and have been shown to be feasible for certain types of reactors.⁽⁴⁾ Ideally, a cermet fuel would retain the mechanical and thermal properties and core-cladding metallurgical bond provided by the metallic matrix of dispersion fuels but would contain higher fuel loadings. Unfortunately, the reduction in matrix volume introduces fabrication problems not encountered with dispersion fuels. Consequently, the present program had two primary objectives: (1) to develop fabrication techniques for producing highly loaded UO_2 cermets, and (2) to demonstrate that such cermets are superior to UO_2 in the properties of interest.

On initiation of the program, cermet compositions containing UO_2 loadings of 60 volume per cent and higher were selected for study. A minimum-density specification of 90 per cent of theoretical was adopted for candidate compositions. Matrix materials of chromium, molybdenum, and niobium were chosen for study because of their compatibility with UO_2 , their moderate-to-high melting temperatures, and the possibility of their being used with an appropriate cladding material. Stainless steel was also selected for investigation because of its compatibility with UO_2 , its cladding possibilities, and its known physical and mechanical properties.

Mixing and blending techniques were investigated for the various powder mixes. Optimum particle sizes and shapes as well as binders were selected on the basis of as-fabricated microstructures. Compacting studies were conducted to select the best compacting conditions.

Sintering, hot-press-forging, and gas-pressure-bonding fabrication techniques were investigated to select a method of producing simple shapes of high density at reasonable cost.

Mechanical properties of fabricated cermets were obtained by bend and compression tests to determine modulus of rupture, compressive strength, Poisson's ratio, and modulus of elasticity. Thermal-conductivity, thermal-expansion, and electrical-resistivity data were also obtained.

FABRICATION STUDIES

Objectives

The objectives of the fabrication studies were to evaluate potential methods for preparing cermets having a minimum UO_2 fuel loading of 60 volume per cent and a minimum density of 90 per cent of theoretical. When satisfactory methods were developed,

(1) References are at end of report.

specimens of such a cermet were to be prepared for measurements of thermal and mechanical properties. These data would allow direct comparison of the cermet with bulk UO_2 .

To meet the objectives, it was necessary to select promising matrix metals for evaluation. To be suitable for this application, such metals should have a high melting point and be compatible with UO_2 at moderate-to-high temperatures. Satisfactory methods of preparing green compacts to obtain homogeneous cermets had to be established and investigations of potential fabrication techniques initiated. After selection of a fabrication method, cermets had to be prepared for the property studies.

Materials

Matrix metals chosen for evaluation for UO_2 cermet preparation, selected on the basis of available nuclear and thermodynamic data and compatibility studies, were chromium, molybdenum, niobium, and Type 302B stainless steel. All metals selected for evaluation are commercially available and are compatible with at least some of the commonly used cladding materials. Although stainless steel has a relatively high cross section, it was chosen for evaluation because of its many known physical and mechanical properties as well as its known use as a reactor material.

The particle sizes of all matrix metals were confined to minus 325 mesh. To determine the effect, if any, of UO_2 shape upon the fabricated microstructure, both hydrothermal and spherical oxide powders were evaluated. Table 1 shows the typical analyses of the materials chosen for cermet fabrication studies. Sizing of the UO_2 was done by screening in standard Tyler powder screens.

Evaluation Methods

Density measurements of fabricated cermets were made by measuring the volume and weighing. These measurements, combined with microstructure studies, were used to evaluate compositional and fabrication variables in the early phases of work. As the effect of fabrication and composition variables was established, and test specimens became available, evaluations were also made on the basis of results obtained from physical- and mechanical-property measurements.

Preparation of Green Compacts

In preparing green cores of materials having a considerable density difference, as was the case with the UO_2 and the matrix metals chosen for investigation, it is necessary to establish mixing conditions to obtain homogeneous blends. The effect of mixing time and powder properties must be determined. Since the cores are largely UO_2 , the compacting pressure and additions of dispersants and binders have to be studied in order that a high-strength powder compact is obtained.

Blends of 60 to 90 volume per cent UO_2 were prepared with the various matrix metals and allowed to mix in a standard V-type mixer for periods up to 2-1/2 hr to

TABLE 1. TYPICAL ANALYSES OF MATERIALS USED TO PREPARE CERMETS

Material	Analyzed Impurity Content ^(a) , w/o																			Particle Porosity, volume per cent	
	Ti	Fe	Cr	Ni	Mo	Si	Mn	Mg	Cu	Co	Al	Ca	C	S	P	Li	Gd	O ₂	H ₂		N ₂
Electrolytic chromium	—	0.01	—	N.D.	N.D.	0.001	0.005	0.005	0.01	N.D.	0.02	N.D.	0.05	0.021	0.002	N.D.	N.D.	0.7110	0.0150	<0.007	Nil
Molybdenum	—	0.01	N.D.	0.01	—	0.001	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	0.01	0.003	0.006	—	—	0.2770	0.0031	0.0900	Nil
Type 302B stainless	—	—	18.94	8.77	—	2.36	0.98	—	—	—	—	—	0.08	0.028	0.013	—	—	—	—	—	Nil
Niobium	—	—	—	—	—	—	—	—	—	—	—	—	0.13	—	—	—	—	—	—	—	Nil
Hydrothermal UO ₂ ^(b)	0.1-1.0	—	<0.01	—	—	<0.01	<0.01	—	<0.01	—	<0.01	<0.01	—	—	—	—	—	—	—	—	Nil
Spherical UO ₂ ^(c)	—	—	—	—	0.015	0.015	—	—	—	0.001	0.02	—	—	—	—	0.0005	0.001	—	—	—	2.5

(a) N.D. = Not detected; dashes indicate that no analysis was made for the element.

(b) Oxygen/uranium ratio was 2.010.

(c) Contains 1 w/o boron.

determine what effect mixing time had upon the homogeneity of the mix. Standard twin-shell V-mixers were used in all mixing studies because of their high efficiency in this application. The effect of UO_2 powder size was studied through the range of minus 100 to 325 mesh. The effect of the addition of up to 1 w/o of a nonmetallic lubricant was also studied.

Initial evaluation of the mixing techniques was made by visual examination. After satisfactory appearing blends were obtained the powder blends were cold compacted and fabricated by hot-press forging. Microstructure evaluations were then made on the fabricated cores to determine optimum blending methods.

A previously determined green compacting pressure of 30 tsi was used in preparing all powder cores⁽⁵⁾, to prevent excessive die wear, maintain minimum UO_2 powder crushing, and obtain a satisfactory compact. All green compacting was achieved with a single-acting powder die. Zinc stearate was employed as the die lubricant. Diameter-to-height ratios of the green-pressed cores were 1 or greater.

It was found that homogeneous molybdenum-matrix cermets could be prepared by mixing UO_2 and molybdenum powders for 2 hr in a standard twin-shell V-type mixer and then cold compacting by the procedure outlined above. No binder was employed. The microstructure of a molybdenum-80 volume per cent UO_2 cermet prepared by this technique and then gas-pressure bonded is shown in Figure 1. It is apparent that the gray UO_2 particles are discontinuous whereas the molybdenum matrix is a continuous phase.

FIGURE 1. DISPERSION OBTAINED BY MIXING 80 VOLUME PER CENT UO_2 -MOLYBDENUM DRY AND CONSOLIDATING BY GAS-PRESSURE BONDING

While this procedure produced UO_2 -molybdenum cermets exhibiting excellent homogeneity, the green-pressed compacts were somewhat less durable than desirable for subsequent fabrication operations. In order to obtain more robust UO_2 -molybdenum green-pressed cermets, less than 1 w/o ethylene glycol was added after dry mixing for 2 hr, and the mix was allowed to blend an additional 2 hr before consolidation by cold compacting.

Chromium, niobium, and stainless steel- UO_2 cermets were very similar in mixing characteristics and will be discussed as a group. Standard 80 volume per cent UO_2 -metal mixes were prepared and mixed dry in a twin-shell V-type mixer for times up to 2-1/2 hr. Improvements in the homogeneity of the blends with longer mixing times could be detected by visual examination for mixing times up to 2 hr. Additional mixing time

had no noticeable effect. Unfortunately these powders showed a tendency toward segregation of the two phases during weighing and pressing operations.

Schwarzkopf⁽⁶⁾ has suggested the use of a nonmetallic lubricant when blending metallic with nonmetallic powders to improve the compressing characteristics by reducing the interparticle friction and friction between particles and die walls. It also seems likely that a properly selected lubricant could act as a dispersant and help coat the UO_2 particles with metal powder during blending. This should retard segregation during subsequent handling. The various lubricants studied in preparing UO_2 -metal cermets in the present program included ethylene glycol, Ceremul "C", and camphor-alcohol solution. The camphor-alcohol solution used was prepared by dissolving 1 oz of camphor in 600 cm^3 of methyl alcohol.

The lubricants were added in concentrations of up to 1 w/o to the powder blends that had been mixed dry for 2 hr, and the powder was allowed to mix an additional 2 hr. Additions of less than 1 w/o ethylene glycol were found to give the most satisfactory results.

A second method of preparing satisfactory blends of the cermets involved coating the UO_2 with camphor by stirring the powder in 3 cm^3 of the camphor-alcohol solution per 100 g of UO_2 . The alcohol was then evaporated away, and the UO_2 was screened through a 100-mesh powder screen to break up any UO_2 agglomerates. The screened UO_2 and the proper proportion of metal powder were then blended for 1 hr. Then 1 cm^3 of the camphor-alcohol solution per 100 g of mix was added, followed by an additional 2 hr of blending. If the powder blend became too dry during subsequent weighing and pressing operations, segregation occurred. If the mix was made too wet by the addition of camphor-alcohol solution, the metal segregated by balling during additional mixing.

To determine the optimum particle size of UO_2 for blending and green compacting, cermet blends containing UO_2 in the range of minus 100 plus 325 mesh were prepared with all matrix metals. The blended powders were cold compacted at 30 tsi, and density measurements were made. Highest densities were obtained using minus 100 plus 140-mesh UO_2 in all cases. This indicates that the coarser UO_2 results in closer packing and probably better mixing characteristics.

The particle shape was found to have a considerable effect upon the dispersions obtained during subsequent fabrication operations. Figure 2 shows the dispersions obtained in 80 volume per cent UO_2 -Type 302B stainless steel cermets using minus 100 plus 140-mesh spherical UO_2 in one case and minus 100 plus 140-mesh hydrothermal UO_2 in the other. Both mixes were prepared in the same way using the same proportion of ethylene glycol dispersant. Subsequent fabrication for densification was by gas-pressure bonding for 3 hr at 10,000 psi at 2300 F. Gas-pressure-bonding techniques will be described in detail in a later section. It can be seen in Figure 2 that the stainless steel matrix is more continuous in the microstructure containing spherical UO_2 .

Investigation of Fabrication Techniques

Sintering and various forms of hot pressing were the only methods investigated for preparing dense cermet bodies since these methods should provide the highest probability for successfully maintaining a continuous metallic matrix during fabrication.

100X

As Polished

RM11684

a. Hydrothermal UO_2

100X

As Polished

RM15248

b. Spherical UO_2

FIGURE 2. EFFECT OF UO_2 PARTICLE SHAPE ON 80 VOLUME PER CENT UO_2 -STAINLESS STEEL DISPERSIONS

The dark phase is UO_2 , the light phase is stainless steel.

Sintering

Sintering studies were conducted on various fuel-matrix combinations to determine the feasibility of producing dense cermets by this technique. Cermets of 80 volume per cent UO_2 dispersed in the different matrix metals were compacted and sintered for various times at high temperatures in a vacuum. The UO_2 -stainless steel cermets were also sintered in dry hydrogen. Minus 140 plus 200-mesh spherical UO_2 was used.

As has been reported⁽⁵⁾, sintering of UO_2 -stainless steel in dry hydrogen at 2200 F results in a density loss. Vacuum sintering of UO_2 -stainless steel above the melting point of stainless steel also results in bodies having a low density since the stainless steel does not wet the UO_2 and migrates from the compact during sintering, forming spheres of metal on the compact surface.

Vacuum sintering of 80 volume per cent spherical UO_2 -chromium, -molybdenum, and -niobium green-pressed cermets resulted in little or no densification. Typical results are listed in Table 2. Microstructures of the sintered cores listed in Table 2 are shown in Figure 3. It can be seen in these photomicrographs that, except possibly for the molybdenum cermet, no wetting of the UO_2 particles by the matrix metals occurred. Shrinkage and weight losses also occurred in all cores during the 1/2-hr sintering treatment. Additional sintering for periods up to 2 hr at the temperatures listed in Table 2 intensified the weight loss with no further shrinkage, resulting in a density decrease.

TABLE 2. EFFECT OF 1/2-HR VACUUM SINTERING ON THE DENSITY OF 80 VOLUME PER CENT UO_2 CERMETS

Metal Matrix	Sintering Temperature, F	Density, per cent of theoretical	
		Green	Sintered
Chromium	2400	70.4	71.9
Molybdenum	3500	73.3	75.2
Niobium	3190	73.6	74.1

Hot-Press Forging

Cursory fabrication studies indicated that the hot-press-forging process was a potential method for preparing cermets having densities 90 per cent of theoretical or greater. In this process a green compact is sealed into a picture frame, covered, and the entire assembly, core and frame, is heated and reduced in thickness on a press-forging machine. The process should be representative of conventional hot pressing, however, problems of contamination and equipment construction and maintenance usually associated with hot pressing are avoided during the materials evaluation. Also for some fuel shapes, particularly plates, hot-press forging itself might well be competitive with conventional hot pressing. It was decided that a more comprehensive investigation of the process should be conducted than was done with sintering to determine what effect, if any, such variables as temperature, forging reductions, and UO_2 shape and size had on the density and microstructure of the various cermets. Studies were also conducted in which metal-coated UO_2 powder was employed in an attempt to improve dispersion

100X

As Polished

RM16549

a. Molybdenum Matrix

100X

As Polished

RM16550

b. Niobium Matrix

100X

As Polished

RM16551

c. Chromium Matrix

FIGURE 3. STRUCTURES OF 80 VOLUME PER CENT UO_2 CERMETS VACUUM SINTERED 1/2 HR AT TEMPERATURE THREE-FOURTHS THAT OF MELTING POINT OF MATRIX MATERIAL

structures. Pack-shape studies were conducted to appraise the effect of this variable upon the degree of cracking of the cermet occurring during fabrication.

Powder blends were prepared and compacted at 30 tsi to a thickness of 1/4 in. Square and round cores were used. UO_2 particle sizes were varied through the range of minus 100 plus 325 mesh with all matrix metals. Both spherical and hydrothermal UO_2 were employed to detect any effect of particle shape. A study of the use of niobium-coated UO_2 powder to improve the bonding and dispersion characteristics of the cores was undertaken. The UO_2 powder was coated with niobium metal by the vapor-deposition method. The coating process has been described by Oxley, et al. (7)

Green-compacted cermets were outgassed in a vacuum at 1200 F to remove binders and residual gases prior to sealing into a 1/4-in.-thick by 2-in.-square or a 2-in.-diameter Type 304 stainless steel picture frame with, respectively, a 1-in.-square or 1-in.-diameter cavity. Powder cores were sealed into the picture-frame packs by welding on 1/8-in.-thick cover plates to each side. Welding was done in an argon-filled tank. The picture frames and cover plates were coated with MgO prior to welding to aid in the removal of compacts after hot-press forging.

The packs were press forged at temperatures of 1900 to 2200 F in a direction parallel with the 1/4-in.-thickness. The packs were heated for 20 min in a furnace at the desired temperature, transferred to the press platen, reduced in thickness to 10 mils over that desired, reheated 10 min, and then reduced to the final thickness. A 27 to 45 per cent reduction in thickness was given to all packs.

Pack design was found to have considerable effect upon the occurrence of cracking in the hot-press-forged cermet. When 2-in.-square frames were used to accommodate a 1-in.-square core, the press-forged cermet was generally cracked diagonally when reductions of 30 per cent were used in press forging. However, when 2-in.-square or 2-in.-diameter frames to accommodate 1-in.-diameter cores were used, cracking of the press-forged cermets was not a problem until reductions of approximately 40 per cent in thickness were achieved. This behavior may be explained by the more uniform restraint offered to lateral flow during the application of pressure by the round core-frame configuration than would be expected from the rectangular core-frame configuration.

It was found that UO_2 cermets can be hot-press forged to densities 90 per cent of theoretical or greater at temperatures of 1900 to 2200 F. As shown in Figure 4, increasing the forging temperature from 1900 to 2200 F had no noticeable effect upon the transverse microstructure.

The specimens shown in Figure 4 contained 80 volume per cent minus 100 plus 140-mesh hydrothermal UO_2 in a niobium matrix. Forging temperatures were 1900 and 2200 F, and the corresponding densities achieved were 90 and 91.9 per cent of theoretical, respectively. Similar results were obtained with chromium, molybdenum, and Type 302B stainless steel matrices.

Reductions of approximately 30 per cent in thickness at 1900 to 2000 F resulted in densities 90 per cent of theoretical for all 80 volume per cent UO_2 cermets with both the 1-in.-square and the 1-in.-diameter cores. However, when temperatures of 2200 F were used for hot-press forging, reductions approaching 40 per cent in thickness were necessary to obtain cermets with densities 90 per cent of theoretical or greater. This

100X

As Polished
a. 1900 F

RM12076

100X

As Polished
b. 2200 F

RM12073

FIGURE 4. EFFECT OF HOT-PRESS-FORGING TEMPERATURE ON UO₂-NIOBIUM CERMETS

behavior is attributed to a decrease with increasing temperature in the restraining force during forging imposed on the cermet core by the stainless steel container.

A study of the effect of UO_2 particles sizes upon the as-press-forged microstructure was made. The UO_2 particle size was varied from minus 100 plus 140 mesh through the minus 270 plus 325-mesh range. In these experiments all hot-press packs were reduced 40 per cent in thickness at 2100 F. It was found that a reduction of the UO_2 particle size to below minus 200 plus 270 mesh resulted in increased porosity within the UO_2 areas and a tendency to form a discontinuous metal matrix. Increasing the UO_2 particle size to above minus 200 plus 270 mesh resulted in increased UO_2 fragmentation and a tendency for the metal matrix to agglomerate. The same results were obtained with chromium, molybdenum, niobium, and stainless steel matrices.

As has been reported in BMI-1282(5) in UO_2 -stainless cermet specimens containing up to 60 volume per cent hydrothermal UO_2 , the UO_2 is usually present as discrete particles or agglomerates of several particles. With this fuel distribution, a strong, continuous stainless steel skeleton is obtained. In this present study continuous skeletons were obtained in specimens containing up to 87 volume per cent UO_2 , but in these higher loadings, the skeletons were not uniform after hot-press forging.

A method of overcoming metal discontinuity with higher loadings of UO_2 was achieved by using niobium-coated UO_2 powder. By controlling the thickness of metal deposited on the UO_2 particles, compositional control can be maintained and metal-to-metal contact is assured during subsequent densification operations.

Figure 5 shows the microstructure of a cermet prepared with niobium-coated UO_2 powder. This specimen had a density 91.6 per cent of theoretical, and contained, nominally, 81 volume per cent UO_2 in the niobium matrix. The minus 100 plus 140-mesh UO_2 -powder was coated with 3 to 7 μ of niobium by vapor-deposition techniques. Hot-press forging was done at 2100 F. It can be seen that in the microstructure shown in Figure 5 the metal phase is extremely uniform and that a perfectly homogeneous dispersion is obtained.

FIGURE 5. CONTINUITY OF METAL PHASE OBTAINED USING NIOBIUM-COATED UO_2 POWDER

Particle shape was found to have a considerable effect upon the homogeneity of the dispersions obtained. Figure 6 shows the effect of UO_2 shape on the microstructures of hot-press-forged cermet. Both specimens contain 80 volume per cent UO_2 dispersed in molybdenum, one containing hydrothermal UO_2 and the other containing spherical UO_2 of the same mesh size. A temperature of 1900 F was used for hot pressing. Densities are 92 per cent of theoretical or greater in both cases. It can be noted that the spherical UO_2 results in a much more uniform dispersion. Similar results were obtained when other matrix metals were used in conjunction with spherical UO_2 .

As would be expected, in hot-press forging or hot pressing, most of the densification of the core occurs in the direction parallel with the direction of pressing (transverse). As shown by the typical photomicrographs shown in Figure 7, cermets prepared by hot-pressing techniques exhibit microstructures in which the UO_2 has been elongated in a direction normal to pressing. No significant differences in this respect were evident among hot-pressed specimens prepared with the four matrix metals.

Pressure-Bonding Studies

Gas-pressure bonding of green cermet cores was investigated to determine the feasibility of preparing dense cermets with high fuel loadings. When it became apparent that the process was capable of producing cermets of high density with desirable microstructures, efforts were centered on producing bodies of the different compositions in shapes desirable for physical and mechanical measurements. Complete evaluations of material and fabrication variables such as the effect of powder sizes on the flow properties during pressure bonding and the effect of pressure-bonding parameters for all the various powder cermets were not made, nor was an evaluation of many types of UO_2 powder made. However, information concerning such factors as the effect of UO_2 loading, pressure-bonding temperature, and specimen geometry on the cermet microstructures was collected. Also, when the matrix metal and cladding used were compatible the possibility of simultaneously densifying and cladding the cermet during gas-pressure bonding was investigated. The effect of UO_2 shape on cermet microstructure was determined, and studies were made to assess the feasibility of obtaining cladding-to-cladding bonds at pressure-bonding conditions suitable for cermet densification.

Description of Process and Apparatus. Gas-pressure bonding utilizes gas pressure at elevated temperatures for the direct densification, cladding, and joining of reactor components. For the present application the components to be bonded are green pressed to size and assembled in a metallic container. The container is evacuated, sealed, and placed inside a high-pressure-gas autoclave, and subjected to a high external gas pressure at elevated temperatures. A pressure of 10,000 psi for a 3-hr time at temperature was used unless otherwise noted.

The specimens were pressure bonded in a 9-in. -ID cold-wall autoclave. A molybdenum resistance heater was located in the center of the autoclave, and the specimens to be bonded were placed in this heater. Several thermocouples were spaced along the length of the specimens to record the temperature gradient. A detailed description of this equipment is given elsewhere in the literature. (8)

100X

As Polished
a. Hydrothermal UO_2

RM12021

100X

As Polished
b. Spherical UO_2

RM13752

FIGURE 6. EFFECT OF UO_2 PARTICLE SHAPE ON THE HOT-PRESS-FORGED MICROSTRUCTURE OF 80 VOLUME PER CENT UO_2 -MOLYBDENUM

100X As Polished RM13753
a. Longitudinal Section, Molybdenum Matrix

100X As Polished RM13752
b. Transverse Section, Molybdenum Matrix

100X As Polished RM13747
c. Longitudinal Section, Chromium Matrix

100X As Polished RM13746
d. Transverse Section, Chromium Matrix

FIGURE 7. TRANSVERSE AND LONGITUDINAL VIEWS OF CERMETS PREPARED BY HOT-PRESS FORGING

Procedure. The gas-pressure-bonding process requires a pressure differential between the inside of the evacuated container and the outside. Two container types were used. One becomes the cladding for the element or assembly, while the other is removed from the element or assembly after bonding and is discarded. The container must be fabricated of a material that will deform at bonding temperature to allow the external pressure to be transmitted uniformly to the components to bring them into intimate contact so that bonding and densification can occur.

Since densification of the cermets was the primary objective of the program and not core-cladding bonding, no effort was made to obtain tubing which would not react with the chromium or molybdenum matrix materials under the pressure-bonding conditions. Type 304 stainless steel tubes were used as a combined container and cladding for rod-type specimens containing cermets having a stainless steel, molybdenum, or chromium matrix. Attempts at using stainless steel containers on niobium-matrix cermets were unsuccessful due to severe iron contamination. Niobium tubing used as a combined container and cladding was not available until late in the program. Therefore, only a few niobium-containing cermets were fabricated. All containers consisted of tubes ranging from 0.470 to 1.010 in. in ID with wall thicknesses ranging from 0.015 to 0.040 in. End plugs were machined 1/8 in. thick from Type 304 stainless steel and niobium to fit the various tubes. In each specimen one of these end plugs was drilled to accommodate an evacuation tube.

In preparing a specimen for bonding, all parts were degreased, and the end plug without the evacuation tube was Heliarc welded into the tube. Next, the tube was put through a wash cycle and loaded with cold-pressed pellets. Then the other end plug was welded into place. Stainless steel end plugs were welded in an argon-filled tank. Niobium tubes and end plugs were electron-beam welded.

Containers for flat-plate specimens were fabricated of Type 304 stainless steel. In cross section these containers resemble a swastika. The side plates for these containers were fabricated from 0.018-in. -thick sheet by shearing and forming a 90-deg flange 0.125 in. wide on an edge. The end plugs were sheared from 0.080-in. sheet. A form block 0.002 in. larger than the intended assembly size was fabricated of mild steel. The parts were assembled and clamped into position on the form block after being degreased. After welding the form block was removed, and the container was put through a wash cycle. An assembly was then inserted into the container and the end plug and top were welded into place.

After loading, the container was leak tested under water under 50 to 75 psi of helium. If there were no leaks the container was placed on a vacuum system and evacuated to a pressure of 5×10^{-3} mm of mercury, or less, at 1200 F to remove the lubricant from the cermet core. After cooling the containers were evacuated to a pressure of 5×10^{-3} mm of mercury, or less, and sealed.

Cleaning Techniques. After the stainless steel components had been machined to the desired size, they were pickled in a 10 volume per cent nitric acid-2 volume per cent hydrofluoric acid aqueous solution at a temperature of 120 to 140 F for 2 min and rinsed in cold running water.

Prior to assembly the metal components and containers were scrubbed with a brush in methylethyl ketone, transferred immediately into 200-proof methyl alcohol, removed, and blown dry.

Molybdenum and niobium claddings used on flat-plate specimens were pickled, respectively, in 65 volume per cent nitric acid-34 volume per cent distilled water, and 65 volume per cent nitric acid-35 volume per cent hydrofluoric acid and rinsed in water prior to degreasing in methylethyl ketone.

Clean rubber gloves were worn during the cleaning, drying, and assembling operations to prevent recontamination of the cleaned surfaces. The components were assembled immediately after cleaning.

Results. Table 3 is a compilation of the effects of material and process variables on the fabricated density of UO_2 cermet rods prepared by gas-pressure bonding at various temperatures for 3 hr at 10,000 psi of helium gas pressure.

Except for one specimen, core diameters ranged from 0.470 to 0.760 in. No variation was noted in the pressure-bonded densities achieved when core diameters were varied within this range. However, a 2 to 3 per cent loss in density was noted when the diameter was increased to 1.01 in. Containers or cladding walls were varied from 10 to 40 mils in thickness with no noticeable effect upon the gas-pressure-bonded densities.

By comparing the data listed for Specimens 1, 4, TC-82, TC-90, and UO_2 -1 and UO_2 -2 in Table 3, it will be noted that with lower fuel loadings higher densities were achieved under the same gas-pressure-bonding conditions. This behavior results from the larger volume of material capable of plastic flow at the bonding temperature.

It is also obvious from the data shown in Table 3 that a temperature of 2200 to 2300 F is required to obtain cermet densities of 90 per cent of theoretical or greater when gas-pressure bonding cermets containing 80 volume per cent UO_2 in any of the four matrix metals.

The experiments demonstrated that tube-type cermet cores can be densified and clad by pressure bonding while maintaining the diameter to tolerances of ± 0.0015 in. or better if cermet green-core densities are 70 per cent of theoretical or greater. Sound metallurgical bonds were obtained between stainless steel-stainless steel, molybdenum-molybdenum, and niobium-niobium at temperatures generally employed for densifying UO_2 cermets. Figure 8 shows the interface obtained in a Type 304 stainless steel couple pressure bonded for 3 hr at 10,000 psi at a temperature of 2100 F. In addition, Figure 8 shows bonds between molybdenum-molybdenum and niobium-niobium couples after pressure bonding for 3 hr at 10,000 psi at a temperature of 2300 F. All three of these typical specimens exhibit grain growth across the bond interface.

By the use of green-pressed cores of the cladding material for spacers and end plugs a uniformly clad tube-type cermet can be obtained. Figure 9 shows an example of the densification and bonding of a green-pressed core of niobium used as an end plug in preparing an 80 volume per cent UO_2 -niobium cermet clad with niobium. Both the niobium end plug and the cermet cores had a green density of 73 per cent of theoretical before gas-pressure bonding at 2300 F. It can be noted that the green-pressed niobium core shown above the interface in Figure 9 was both densified and metallurgically bonded to the cermet fuel core and the niobium cladding. Similar results can be expected by using green-pressed metal cores for the side pieces of flat-plate cermet-clad fuel elements.

TABLE 3. EFFECT OF VARIABLES ON UO₂ CERMET RODS PREPARED BY GAS-PRESSURE BONDING

Matrix Metal	Description of Fuel Loading			Specimen	Pressure-Bonding Temperature, F	Density, per cent of theoretical	
	UO ₂ Type	Particle Size, mesh	Amount, volume per cent			Green	Fabricated
Stainless steel	Hydrothermal	-100+140	60	1	2100	72.0	91.7
			70	TC-81	2300	--	97.0
			80	2	2300	75.4	95.2
			80	TC-102	2300	75.0	98.4
			80	TC-80	2300	67.8	95.5
			85	3	2300	76.9	96.9
			90	4	2100	75.4	82.0
	Spherical	-100+140	80	RSS-1	2300	74.0	97.4
			80	RSS-2	2200	74.0	94.4
			80	TC-103	2300	72.0	97.2
		-100+200	80	RSS	2300	74.0	96.5
Molybdenum	Hydrothermal	-100+140	70	TC-82	2300	--	91.7
			80	90 ^(a)	2300	72.0	86.8
			80	TC-90	2400	--	91.1
	Spherical	-100+140	80	TC-105	2350	72.0	94.4
			80	RMo-1	2300	75.6	90.7
			80	RMo-2	2200	75.6	88.5
		-140+200	80	RMo	2300	73.7	91.6
Chromium	Spherical	-100+140	80	RCr-2	2200	75.0	95.5
			80	RCr-1	2300	75.0	97.0
			80	TC-104	2300	74.0	97.1
		-140+200	80	RCr	2300	74.7	96.5
Niobium	Spherical	-100+140	80	5	2100	--	84.9 ^(b)
			80 ^(c)	TC-115	2100	76.4	85.3
		-140+200	80	RNb-1	2350	74.0	91.1
			80	RNb	2350	74.0	92.0
	Hydrothermal	-140+200	80 ^(c)	TC-130	2350	73.0	93.5
None	Hydrothermal	-100+140	--	PBDS-7	2100	76.9	81.0
			--	PBDS-7A	2350	80.7	89.4
	Spherical	-200+325	--	UO ₂ -1	2300	76.0	82.6
			--	UO ₂ -2	2300	76.0	80.7

(a) Green-core diameter was 1.01 in.

(b) Estimated.

(c) UO₂ powder was coated with niobium by vapor deposition.

Interface

100X

Etchant: Modified Murakami

N66187

a. Molybdenum

Interface

100X

Etchant: 50-50-3 Parts Lactic- HNO_3 -HF

N66607

b. Niobium

Interface

50X

Etchant: 30-30-12 Parts HCl -Glycerin- HNO_3 RM15174

c. Stainless Steel

FIGURE 8. METALLURGICAL BONDING OF METAL INTERFACES BY GAS-PRESSURE BONDING

The molybdenum and niobium specimens were bonded 3 hr at 2300 F and 10,000 psi, the stainless steel specimen was bonded 3 hr at 2100 F and 10,000 psi.

100X Etchant: 50-50-3 Parts Lactic- RM16539
HNO₃-HF

FIGURE 9. GREEN-PRESSED NIOBIUM END PLUG DENSIFIED AND BONDED BY GAS-PRESSURE BONDING AT 2300 F

As shown in Figure 10, a homogeneous microstructure is obtained in both the transverse and longitudinal sections when cermets are densified by gas-pressure bonding. The shape of the fuel particles significantly influences the homogeneity obtained, however. Figure 11 shows the vast improvement in microstructure obtained by using spherical UO₂ as compared with hydrothermal UO₂. Both specimens contain 80 volume per cent minus 100 plus 140-mesh UO₂ in a stainless steel matrix. Both specimens were gas-pressure bonded at 2300 F to densities 95 to 97 per cent of theoretical. Similar improvements were noted when spherical UO₂ was employed with other matrix metals.

As shown by Specimen TC-130 in Figure 12, sound metallurgical bonding can be obtained between the core and cladding by gas-pressure bonding. In addition, as Figure 12 shows, a more uniform dispersion is obtained by the use of niobium-coated UO₂ particles. The specimen was prepared by compacting minus 140 plus 200-mesh hydrothermal UO₂ which had previously been coated with 20 volume per cent niobium by the vapor-deposition method. Niobium tubing was used as cladding material, and pressure bonding was done at 2350 F. The pressure-bonded core exhibited a density of 93.5 per cent of theoretical.

As might be expected, considerable difficulty was encountered in pressing thin-section cermets of satisfactory green strength for the preparation of flat-plate fuel elements. Attempts were made to gas-pressure bond 1 by 1 by 0.100-in. green-pressed 80 volume per cent UO₂ cermets in swastika-type containers previously described. The green-pressed cores were extremely fragile and could not be assembled into the pressure-bonding containers without breakage. The extreme fragility of the green-pressed cores was overcome by vacuum sintering the compacts for 1/2 hr at 2300 to 2500 F. This resulted in a core which could be handled without difficulty; however, considerable breakage and core cracking was encountered upon ejecting the cores from the die after green pressing. Breakage could be greatly reduced by increasing the thickness

to approximately 0.200 in. A typical microstructure of cermet specimens densified by gas-pressure bonding is shown by the transverse and the longitudinal sections presented in Figure 13. The specimen was prepared by green pressing an 80 volume per cent minus 140 plus 200-mesh UO_2 -molybdenum mix at 30 tsi to 1 by 1 by 0.100 in., sintering, and gas-pressure bonding at 2300 F. The uniform hydrostatic pressure applied during gas-pressure bonding deformed the core in all directions, preventing flattening of the UO_2 into platelets as was the case when the cermets were fabricated by hot-press-forging techniques. Similar microstructures were obtained when using other matrix metals.

Table 4 presents a listing of 80 volume per cent UO_2 1 by 1 by 0.100-in. cermets gas-pressure bonded under various conditions. It will be noted by comparing specimens in Tables 3 and 4 that similar densities were achieved by gas-pressure bonding cermets in either the rod or flat-plate-type configurations.

Discussion

Sintering was demonstrated to be an infeasible method of producing high-density UO_2 cermets, although sintering was conducted at temperatures high enough for UO_2 sintering. Although not completely investigated, the low densities achieved by sintering were felt to be due to little or no wetting of UO_2 by the metals tried. In addition, the large UO_2 sizes required for obtaining uniformly dense cermets are not desirable for sintering.

Densities of 90 per cent of theoretical or greater can be achieved by hot-press forging cermets containing 60 to 90 volume per cent UO_2 ; however, a considerable limitation is placed upon the size of the cermets due to the high compacting pressures required to deform core and frame. Cores prepared in this manner would require machining to size before cladding operations for reactor use. Furthermore, the inhomogeneous microstructures would have to be taken into consideration during design of a fuel element. All things considered, it appears that the hot-press-forging technique would be uneconomical for producing cermet cores for reactor fuel elements when compared with alternate procedures.

From the studies conducted with gas-pressure-bonding techniques for producing physical- and mechanical-measurement specimens, it has been noted that little limitation is placed upon the shape of the specimens which can be fabricated to high density. Cermet rods 1 in. in diameter by 3 in. long have been densified and bonded while maintaining close dimensional control. The feasibility of preparing specimens with uniform cross sections by the use of green-pressed metal cladding components has been demonstrated as well as the feasibility of densifying and cladding cermets in one operation. Uniform, homogeneous microstructures can be obtained by mixing powders or by using vapor-deposited metal-coated UO_2 and densifying by the gas-pressure-bonding technique.

100X As Polished RM16425
a. Specimen RSS-1, Transverse

100X As Polished RM16424
b. Specimen RSS-1, Longitudinal

100X As Polished RM16447
c. Specimen RCr-1, Transverse

100X As Polished RM16436
d. Specimen RCr-1, Longitudinal

FIGURE 10. TRANSVERSE AND LONGITUDINAL SECTIONS OF UO_2 CERMETS PREPARED BY GAS-PRESSURE BONDING

100X As Polished RM16443
e. Specimen RMo-1, Transverse

100X As Polished RM16444
f. Specimen RMo-1, Longitudinal

100X As Polished RM16541
g. Specimen RNb-1, Transverse

100X As Polished RM16540
h. Specimen RNb-1, Longitudinal

FIGURE 10. (Continued)

100X

As Polished

RM12077

a. Hydrothermal UO_2

100X

As Polished

RM16425

b. Spherical UO_2

FIGURE 11. EFFECT OF UO_2 SHAPE ON UO_2 -STAINLESS STEEL CERMET MICROSTRUCTURES PREPARED BY GAS-PRESSURE BONDING

250X Etchant: 50-50-3 Parts Lactic-HNO₃-HF RM16548

FIGURE 12. NIOBIUM-COATED UO₂ DENSIFIED AND CLAD WITH NIOBIUM BY GAS-PRESSURE BONDING

FIGURE 13. MICROSTRUCTURE OF AN 80 VOLUME PER CENT UO_2 -MOLYBDENUM-FLAT PLATE CERMET AFTER GAS-PRESSURE BONDING AT 2300 F

TABLE 4. FLAT-PLATE 80 VOLUME PER CENT UO_2 CERMETS
DENSIFIED BY GAS-PRESSURE-BONDING

Matrix Metal	Specimen ^(a)	Pressure-Bonding Temperature, F	Density, per cent of theoretical	
			Sintered	Pressure Bonded
Stainless steel	SS-3	2300	74.6	95.6
	SS-4	2250	72.0	92.5
	SS-5	2250	72.7	95.0
Molybdenum	Mo-2	2300	71.8	89.0
	Mo-3	2300	72.9	90.0
	Mo-5	2250	--	88.4
Chromium	Cr-2	2100	71.5	93.0 ^(b)
	Cr-3	2200	71.5	95.0 ^(b)
Niobium	Nb-3	2200	73.4	83.2
	NB	2385	--	81.4 ^(c)

(a) All specimens were prepared with minus 140 plus 200-mesh spherical UO_2 except Specimen Nb-3, which was prepared with minus 100 plus 200-mesh spherical UO_2 , and Specimen Nb, which was prepared with minus 140 plus 200-mesh hydrothermal UO_2 .

(b) Estimated from microstructure.

(c) Can be believed to have leaked during pressure bonding.

MECHANICAL PROPERTIES

In the evaluation of any material proposed for use as a fuel in nuclear reactors, the mechanical properties of the material are an important consideration. For example, the values for modulus of elasticity and Poisson's ratio are essential to the design engineer for the calculation of thermal stresses in clad fuel elements. The strength and ductility measurements of the fuel core prescribe limits beyond which integral behavior cannot be expected. In many instances cracks or discontinuities resulting from localized exhaustion of ductility cannot be tolerated because of the excessive heat generated at such discontinuities. The possibility of catastrophic failure of the entire clad fuel element also exists. Such failure could be nucleated by cracks in the fuel core.

Dynamic properties such as those measured by fatigue tests, creep tests, and thermal-cycle tests assist in evaluating the mechanical life of the proposed fuel as opposed to its life as an efficient nuclear fuel. Many other criteria by which fuel elements are judged, such as fission-gas retention and swelling, are also closely related to the mechanical properties of the fuel.

In view of the importance of mechanical properties in the evaluation of fuel materials, mechanical tests were performed on cermet of various compositions. The tests were limited to those for room-temperature compression and modulus of rupture.

Compression Tests

Compression tests were performed using a 60,000-lb-capacity Baldwin-Lima-Hamilton universal testing machine. For each specimen strain values were obtained from five SR-4 strain gages, three oriented in an axial direction, and two circumferentially oriented to provide transverse strain measurements.

The specimens tested were prepared by gas-pressure-bonding techniques. The cladding was ground from each cermet so that a smooth surface could be obtained. Specimens were 3/8 in. in diameter by 1-1/8 in. in length. Table 5 is a tabulation of the compositions and densities of the specimens employed in the compression tests. Spherical UO_2 was used in all specimens. Measurements in compression were not made on a niobium-matrix cermet. Figure 14 shows the microstructures of the specimens tested in compression.

TABLE 5. COMPOSITION AND DENSITY OF UO_2 CERMETS USED IN COMPRESSION TESTING

Specimen	UO_2 Content, volume per cent	Mesh Size of UO_2	Matrix Metal	Density, per cent of theoretical
RSS	80	-140+200	Stainless steel	96.5
RCr-1	80	-100+140	Chromium	97.0
RMo-1	80	-100+140	Molybdenum	90.7

50X

As Polished

RM16430

a. Specimen RSS

50X

As Polished

RM16446

b. Specimen RCr-1

50X

As Polished

RM16445

c. Specimen RMo-1

FIGURE 14. MICROSTRUCTURES OF 80 VOLUME PER CENT UO_2 CERMETS TESTED IN COMPRESSION

The resulting data are plotted in Figures 15, 16, and 17. It will be noted that values for Poisson's ratio are also given. These values were obtained in the usual manner by dividing the average transverse strain by the average longitudinal strain.

Figure 15, which presents data obtained from the test on Specimen RSS, shows a gradual rise in Poisson's ratio with increasing strain in the range of stress below the proportional limit. Since Poisson's ratio is generally a constant for elastic strains, this behavior seems to indicate that permanent deformation was occurring at stresses below the apparent proportional limit. This observation was also supported by the appearance of permanent strains during the alignment of this specimen. The maximum stresses imposed during alignment were well below the proportional limit of this material.

During the tests of Specimens RCr-1 and RMo-1, as can be seen by the results shown in Figures 16 and 17, permanent strains below the proportional limit were not observed even though the alignment stresses imposed were higher than those on Specimen RSS.

The molybdenum matrix specimen had the lowest strength of the three specimens tested. As expected, this specimen also had the lowest theoretical density.

Bend Tests

Bend tests were conducted on three types of modulus-of-rupture specimens. Initially, specimens were prepared by grinding 0.090 by 1-1/8-in. specimens from hot-press-forged cermets and 0.070 by 0.150 by 1-1/8-in. specimens from gas-pressure-bonded flat-plate cores. Bending of the specimens was done on a 1000-lb-capacity Amsler testing machine at room temperature. Specimens were loaded in simple bending with the central concentrated load being applied through a 1/8-in.-radius steel pin. The rate of loading was approximately 100 lb per min. The span was 0.83 in. Table 6 shows the moduli of rupture obtained from specimens ground from flat-plate gas-pressure-bonded samples containing 80 volume per cent UO_2 . Minus 140 plus 200-mesh spherical UO_2 was used. Figure 18 shows typical microstructures of the transverse sections of the specimens tested. UO_2 stainless steel cermets of varying UO_2 loading prepared by hot-press forging and grinding have been tested and previously reported.⁽⁵⁾ In addition, an 80 volume per cent UO_2 -molybdenum cermet having a density of 93.6 per cent of theoretical was tested and found to have a modulus of rupture of 22,200 psi. The specimen was prepared by hot-press forging.

Because of the difficulty of grinding rectangular cermets without chipping or cracking, it was decided to fabricate round test specimens by gas-pressure bonding in an attempt to obtain more desirable surfaces by centerless grinding. Modulus-of-rupture testing was done on a 60,000-lb-capacity Baldwin-Lima-Hamilton universal testing machine. Specimens were loaded in simple bending with the central concentrated load being applied through a 1/8-in.-radius steel pin. The rate of loading was approximately 100 lb per min and the span of loading was 2 in.

The specimens were 0.375 in. in diameter by 2.25 in. in length and contained 80 volume per cent spherical UO_2 . Table 7 presents a description of specimens and

FIGURE 15. COMPRESSION-TEST RESULTS OF SPECIMEN RSS

FIGURE 16. COMPRESSION-TEST RESULTS OF SPECIMEN RCr-1

FIGURE 17. COMPRESSION TEST RESULTS OF SPECIMEN RMo-1

TABLE 6. MODULUS-OF-RUPTURE VALUES OBTAINED ON SPECIMENS
PREPARED BY GAS-PRESSURE BONDING

Matrix Metal	Specimen	Density, per cent of theoretical	Measured Modulus of Rupture, psi	Specimen Appearance
Molybdenum	Mo-2-2	89	12,500	Edges chipped
	Mo-2-4	89	15,600	Good
	Mo-3-1	90	12,000	Chipped
	Mo-3-2	90	10,800	Chipped
	Mo-5-1	88.4	11,000	Chipped
	Mo-5-4	88.4	10,500	Good
Stainless steel	SS-2-1	96	14,200	Chipped
	SS-2-3	96	14,500	Chipped
	SS-2-4	96	11,500	Chipped
	SS-3-1	95	12,900	Chipped
	SS-3-2	95	10,600	Chipped
	SS-3-4	95	5,120	Chipped
	SS-4-2	92	11,800	Chipped
	SS-4-4	92	10,100	Chipped
	SS-5-1	95	14,900	Chipped
	SS-5-2	95	15,400	Chipped
	SS-5-4	95	14,300	Chipped

100X

As Polished

RM16278

a. Stainless Steel Matrix

100X

As Polished

RM16272

b. Molybdenum Matrix

FIGURE 18. TYPICAL MICROSTRUCTURES OF FLAT-PLATE MODULUS-OF-RUPTURE SPECIMENS PREPARED BY GAS-PRESSURE BONDING

TABLE 7. DESCRIPTION OF ROD-TYPE CERMETS AND THEIR
MEASURED MODULUS OF RUPTURE

Matrix Metal	Specimen	Mesh Size of UO_2	Density, per cent of theoretical	Modulus of Rupture, psi
Molybdenum	RMo	-140+200	91.6	12,000(a)
	RMo-1	-100+140	90.7	13,800(a)
	RMo-2	-100+140	88.5	12,100
Stainless steel	RSS	-140+200	96.5	18,100
	RSS-1	-100+140	97.4	17,200
	RSS-2	-100+140	94.4	13,300(a)
Chromium	RCr	-140+200	96.5	22,500
	RCr-1	-100+140	97.0	20,600
	RCr-2	-100+140	95.5	21,600

(a) Break definitely originated where two cores were joined.

lists the measured moduli of rupture. Figure 14 shows typical microstructures of the cermets tested. Figure 19 shows specimens before and after testing.

FIGURE 19. UO_2 CERMETS TESTED IN BENDING AND THE TYPE OF FRACTURE RESULTING

It might be of interest to estimate the tensile strength of the various specimens from the bend strengths indicated in the tables and previously reported.⁽⁵⁾ It would be expected from the mechanics of the bend test that the tensile strength of the material will be less than the modulus of rupture for the rectangular beams by the percentage:⁽⁹⁾

$$\frac{17.75}{\left(\frac{L}{t}\right)},$$

where

L = span length

t = height of the beam cross section.

For the rectangular-specimen data shown in Table 6 and previously reported, this correction amounts to a reduction of about 1.5 and 2 per cent, respectively.

As was mentioned previously, the strength would be expected to vary with density to some extent. Figure 20 shows the variation of modulus of rupture with density for the specimens measured containing 74 volume per cent UO_2 dispersed in Type 302B stainless steel. As expected, the tendency for strength to increase with increasing density is observed.

Discussion

Perhaps a word here is in order concerning the mechanical properties of brittle materials. Shanley⁽¹⁰⁾ has pointed out that the design of structures made from brittle materials must be approached from an entirely different viewpoint than that which has

FIGURE 20. VARIATIONS OF MODULUS OF RUPTURE WITH DENSITY FOR 74 VOLUME PER CENT UO_2 -STAINLESS STEEL CERMETS

been found satisfactory for ductile materials. This same philosophy will be necessary in analyzing the behavior of the UO_2 cermet. In this regard, no fixed value of strength can be ascribed to a material. Instead, a frequency distribution of strength values must be employed to provide the necessary design information, and the ordinary concept of a factor of safety must be replaced with a new criterion, the probability of failure. Also, the number of tests necessary to provide design data are naturally higher than the number which would be satisfactory for a ductile material. In view of this, the data in Tables 6 and 7 and Figures 15, 16, 17, and 20 are being presented not as end values in themselves but as a basis for comparison among the materials being examined.

PHYSICAL PROPERTIES

Among the many important properties of potential reactor fuel materials which have to be evaluated before performance can be estimated are the thermal conductivity and thermal expansion. The reactor in its operation depends directly upon the ability of the fuel element to transfer heat which, in turn, is primarily dependent upon its thermal conductivity over the operating-temperature range. Expansion values are required so that structural integrity of the potential fuel element can be evaluated, and clearances set for mechanical assembly.

Most important, these physical measurements show changes which may take place in the material with temperature and irradiation. The thermal conductivity is a structure-dependent property and depends not only upon the gross features of the material, the phases present and phase distribution, but also upon the atomic structure, the crystal form, and structure defects. Thermal expansion, and the closely related density, is more a bulk property, but it can show changes due to growth, recrystallization, and thermal stresses.

Other physical properties also show these changes, among which is the readily measurable electrical resistivity. In many materials, the resistivity can be correlated with the structure and phase distribution, and with many of the physical properties.

Measurements of thermal conductivity, thermal expansion, and electrical resistivity have been completed on several uranium oxide cermets over the temperature range 100 to 900 C. Specimen description and details are given in Table 8.

Figure 21 shows the microstructure of each specimen used in the physical-property studies.

Thermal Conductivity

Method and Apparatus

The method used in making the thermal-conductivity measurements was essentially the same as the comparative, steady-heat-flow method described by Van Dusen and Shelton⁽¹¹⁾. The method, in brief, consisted in heating one end and measuring the temperature gradients along the specimen, and determining the rate of heat flow through the

TABLE 8. DESCRIPTION OF SPECIMENS USED FOR PHYSICAL-PROPERTY MEASUREMENTS

Specimen ^(a)	Nominal Composition, volume per cent	Density, per cent of theoretical	Physical Properties Measured			
			Thermal Conductivity	Linear Expansion	Electrical Resistivity ^(b)	Electrical Resistivity ^(c)
TC-81	UO ₂ -30 stainless	97.0	X	X	X	--
TC-80	UO ₂ -20 stainless	95.5	X	X	X	--
TC-102	UO ₂ -20 stainless	98.4	X	X	X ^(d)	X
TC-103	UO ₂ -20 stainless	97.2	X	X	(e)	X
TC-82	UO ₂ -30 molybdenum	91.7	X	X	X	--
TC-90	UO ₂ -20 molybdenum	91.1	X	--	X	--
TC-105	UO ₂ -20 molybdenum	94.4	X	X	(e)	X
TC-104	UO ₂ -20 chromium	97.1	X	X	(e)	X
TC-115	UO ₂ -20 niobium ^(f)	85.3	X	--	X	--
TC-130	UO ₂ -20 niobium ^(g)	93.5	X	--	X	--

(a) See Table 3 for fabrication data.

(b) Electrical resistivity measured concurrently with thermal conductivity.

(c) Electrical resistivity measured independently of thermal conductivity.

(d) Not reported.

(e) Not calculated.

(f) Niobium-coated minus 100 plus 140-mesh spherical UO₂.

(g) Niobium-coated minus 140 plus 200-mesh hydrothermal UO₂.

specimen by means of a metal standard of known thermal conductivity attached to the cold end. Radial heat flow into, or away from, the specimen was minimized by thermal insulation and an encircling guard tube in which temperatures were adjusted, as nearly as possible, to match those in the specimen and standard at corresponding levels. The thermal insulation used consisted of bubbled alumina, poured into the annular space between the specimen assembly and the guard cylinder. The specimen was protected by a vacuum of approximately 2×10^{-5} mm of mercury during the measurements.

The temperature gradient was measured by thermocouples of calibrated wire which were wedged in holes spaced along the specimen. Thermocouples were also placed in the standard to measure the heat flow. This permitted the calculation of several values of the thermal conductivity for each thermal equilibrium, each at a different mean temperature.

Generally, measurements were made in steps of increasing temperature to the maximum temperature after which one or more equilibria were obtained at lower temperatures. This duplication of measurements was used as a check on thermocouples and changes which may have taken place in the specimen. The thermal-conductivity measuring process is a week-long heat treatment which is different for each section of the specimen.

The apparatus employed in the measurements is a proven piece of equipment and has been in satisfactory use for several years. Experience has established the relative error between different tests run in the apparatus not to exceed ± 2 per cent. This is the apparatus uncertainty when using the same standard. The absolute error of the thermal-conductivity values is estimated not to exceed ± 5 per cent, the chief uncertainty being the absolute thermal conductivity of the material used as a comparative standard.

To control somewhat the temperature gradient through the specimen-standard assembly and to better control guard-specimen temperature balances, two standard materials were used, Armco iron, the primary standard, and Type 347 stainless steel, the secondary standard. Figure 22 shows the heater block, specimen, and standards in place ready for assembly into the vacuum furnace. Thermocouples are shown in position in the specimen (bottom) and standards.

Results

Table 9 gives the observed thermal-conductivity values for the specimens. The data are plotted in Figures 23 and 24.

The temperature dependency and range in values of the thermal conductivity of the specimens can be seen in Figure 25 in which are also plotted literature values for the matrix metals.

The form of the curve fitted to the observed data was established, in general, from the more extensive data. Specimens TC-115, TC-130, TC-90, and TC-82 could not be fitted to this form. To check the general form of the curve, both Armco iron and Type 347 stainless steel standards were used. These, in effect, established different temperature distributions in the measuring apparatus, causing different balancing conditions. For Specimens TC-102 and TC-103, both of which contained 80 volume

100X As Polished RM12628
a. Specimen TC-81

100X As Polished RM12077
b. Specimen TC-80

100X As Polished RM15246
c. Specimen TC-102

100X As Polished RM15248
d. Specimen TC-103

FIGURE 21. MICROSTRUCTURES OF PHYSICAL-PROPERTY-MEASUREMENT SPECIMENS

100X

As Polished

RM12631

e. Specimen TC-82

100X

As Polished

RM14399

f. Specimen TC-90

100X

As Polished

RM15469

g. Specimen TC-105

100X

As Polished

RM15249

h. Specimen TC-104

100X

As Polished

RM15508

i. Specimen TC-115

100X

As Polished

RM16546

j. Specimen TC-130

FIGURE 21. (Continued)

N68877

FIGURE 22. SPECIMEN APPARATUS ASSEMBLY FOR MEASURING THERMAL CONDUCTIVITY

TABLE 9. EXPERIMENTAL THERMAL CONDUCTIVITY OF UO₂ CERMET SPECIMENS

TC-81		TC-80		TC-102		TC-103		TC-82		TC-90		TC-105		TC-104		TC-115		TC-130		TC-130 (Continued)	
Temperature, C	Thermal Conductivity, w/(cm)(C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)	Temperature, C	Thermal Conductivity, w/(cm) (C)
210	0.08 ₁	226	0.06 ₇	215	0.07 ₃	331	0.07 ₀	210	0.19 ₆	125	0.14 ₀	219	0.17 ₃	413	0.17 ₂	174	0.09 ₂	237	0.09 ₅	267	0.09 ₀
173	0.08 ₀	164	0.06 ₆	160	0.07 ₂	291	0.07 ₅	183	0.21 ₂	106	0.13 ₆	203	0.20 ₆	374	0.14 ₆	124	0.08 ₉	205	0.09 ₆	184	0.09 ₈
423	0.08 ₇	442	0.07 ₂	122	0.07 ₇	245	0.06 ₆	467	0.19 ₉	234	0.12 ₇	185	0.18 ₇	329	0.15 ₈	271	0.08 ₈	177	0.09 ₇	161	0.10 ₃
341	0.08 ₆	320	0.06 ₅	383	0.07 ₉	531	0.08 ₄	404	0.20 ₃	195	0.13 ₀	593	0.18 ₇	654	0.17 ₅	404	0.09 ₀	599	0.08 ₅	140	0.09 ₅
674	0.11 ₅	672	0.08 ₈	302	0.07 ₃	472	0.08 ₅	699	0.20 ₁	374	0.11 ₇	543	0.20 ₀	593	0.16 ₁	457	0.09 ₂	502	0.08 ₇		
559	0.10 ₃	500	0.07 ₄	211	0.07 ₆	401	0.07 ₂	613	0.21 ₃	306	0.12 ₀	486	0.17 ₃	521	0.15 ₄	693	0.09 ₀	417	0.08 ₇		
								Second Measurement													
758	0.12 ₇	192	0.07 ₁	571	0.08 ₀	774	0.10 ₂	384	0.21 ₀	515	0.11 ₂	362	0.17 ₀	249	0.19 ₂	522	0.09 ₂	478	0.08 ₇		
642	0.11 ₃	142	0.06 ₃	454	0.07 ₁	697	0.10 ₂	331	0.17 ₃	419	0.12 ₀	333	0.19 ₄	227	0.13 ₃			405	0.09 ₁		
534	0.10 ₄	739	0.09 ₂	317	0.07 ₀	600	0.08 ₁	683	0.19 ₇	659	0.11 ₂	301	0.17 ₆	201	0.16 ₂			341	0.08 ₇		
441	0.09 ₅	555	0.08 ₀	811	0.10 ₆	896	0.13 ₃	593	0.18 ₃	537	0.11 ₂	870	0.23 ₉	732	0.16 ₆			817	0.09 ₀		
305	0.08 ₆			670	0.09 ₆	815	0.11 ₉	625	0.20 ₃			803	0.22 ₅	667	0.15 ₄			685	0.09 ₁		
248	0.08 ₁			492	0.08 ₁	705	0.09 ₁	542	0.17 ₉			724	0.23 ₆	590	0.14 ₁			570	0.09 ₀		
				940	0.12 ₇	197	0.09 ₅	350	0.22 ₂			318	0.16 ₀	915	0.20 ₂			858	0.09 ₇		
				797	0.11 ₆	169	0.06 ₇	302	0.16 ₃			295	0.16 ₆	840	0.18 ₁			723	0.09 ₅		
				611	0.09 ₄			747	0.21 ₂			271	0.18 ₀	744	0.15 ₅			603	0.09 ₁		
				259	0.06 ₇			654	0.18 ₅			811	0.21 ₄	326	0.17 ₆			652	0.09 ₆		
				203	0.07 ₁							746	0.21 ₂	300	0.14 ₉			552	0.09 ₄		
				145	0.07 ₃							671	0.19 ₉	266	0.12 ₈			463	0.09 ₀		
																		368	0.09 ₅		
																		314	0.09 ₄

FIGURE 23. THERMAL CONDUCTIVITY VERSUS TEMPERATURE FOR UO_2 -STAINLESS STEEL CERMET SPECIMENS

FIGURE 24. THERMAL CONDUCTIVITY VERSUS TEMPERATURE FOR UO_2 CERMET SPECIMENS

FIGURE 25. THERMAL CONDUCTIVITY VERSUS TEMPERATURE FOR UO₂ CERMETS AND THEIR MATRIX METALS

per cent UO_2 in stainless steel, there were no significant differences in the measured values when the different standards were used.

Initially, fabrication techniques limited specimen size to one somewhat smaller than ideal for the apparatus. This imposed problems in temperature balancing and, consequently, increased the error. As experience was gained in fabrication techniques, large sizes could be made. Improvements in microstructure also resulted as can be seen by comparing (a), (b), (e), and (i) in Figure 21 (fabricated early in the program) with (c), (d), (f), (g), (h), and (j) Figure 21 (fabricated later in the program). The error of the mean for these measurements is estimated to be not greater than ± 3 per cent.

From an over-all viewpoint, the data show some variation. While the stainless steel and niobium cermet were reasonably self-consistent in behavior, the molybdenum cermet were not. Nor was there a simple relation between the conductivity of the cermet and their matrix metals.

As a set, the UO_2 -stainless steel specimens were reasonably consistent. Specimens TC-102 and TC-103, both containing 80 volume per cent UO_2 , had no significant difference in conductivity. Specimen TC-80, fabricated earlier in the program, but having the same nominal composition, differed by 8 per cent. This difference may be accounted for by the variation in microstructure resulting from improvements in fabrication. Specimen TC-81, which contained a 10 per cent larger fraction of metal, yielded a conductivity some 15 per cent higher. The conductivities of the UO_2 -stainless steel cermet were roughly 60 per cent that of the matrix metal.

The UO_2 -niobium specimens, TC-115 and TC-130, were also self-consistent. Small differences between the two specimens were not at all significant, and the higher density specimen yielded the slightly higher values. The values of the cermet were roughly 15 per cent that of the matrix metal.

Of all the specimens, the UO_2 -molybdenum set showed the most variation. Specimens TC-82 and TC-105, although differing in metal content by 10 volume per cent, had essentially the same conductivity. Since Specimen TC-105 was fabricated later in the program, this may be explained by the improved microstructures, as shown in Figure 21, resulting from improved fabrication techniques. The thermal conductivity of these cermet was roughly 15 per cent that of the matrix metal.

As can be seen in Figure 25, by comparing Specimen TC-82 with TC-90 and Specimen TC-81 with TC-80 (specimens fabricated early in the program) a boost of 30 to 90 per cent in thermal conductivity has been accomplished by increasing the cermet metal content from 20 to 30 volume per cent.

Perhaps the best qualitative measures of heat transfer of these potential reactor fuel materials is the criterion proposed by Lewis⁽¹⁷⁾, that of the integrated thermal conductivity. It has been used by Canadian workers^(18,19) in evaluating fuel performance and has been extended by Robertson⁽²⁰⁾, who showed its applicability for in-pile use. The integrated conductivity may be looked upon simply as a measure of the conductivity weighed over the whole temperature range.

The method of Lewis has been used primarily to evaluate UO_2 fuel elements, and its applicability has been proven by radiation-damage tests on UO_2 . Radiation-damage tests have not been run on the high-loading cermet, but because of their high UO_2

content, it is considered useful to compare the $\int KdT$ as calculated for the cermet with the value of UO_2 . Two comparisons have been made, as shown in Table 10. In the first case, it is assumed that, in order to obtain high burnups, the temperature cannot exceed a value beyond which the metal has little strength. Very few data are available on the strength of the refractory metals at very high temperatures, but Type 316 stainless steel has adequate strength at $0.7 T_m$, where T_m is the absolute melting range. Therefore, the second column in Table 10 gives values of $\int KdT$ for all materials at $0.7 T_m$ of the low-melting constituent. In the second comparison, it is assumed that the fuel element can withstand temperatures up to a point where center-core melting of the lowest-melting constituent begins. Compared with UO_2 , the heat transfer of all these materials looks most promising.

TABLE 10. $\int KdT$ LEWIS CRITERION OF HEAT TRANSFER AS APPLIED TO UO_2 AND UO_2 CERMETS

Material Composition, volume per cent	$0.7 T_m$, L 275	$0.7 T_m^{(a)}$, C	T_m , L 275	$T_m^{(a)}$, C
UO_2	48	1843	70	2750
UO_2 -20 stainless steel	54	881	120	1375
UO_2 -30 stainless steel	65	881	150	1375
UO_2 -20 niobium	128	1609	210	2415
UO_2 -20 chromium	170	1241	310	1890
UO_2 -20 molybdenum	367	1752	620	2620

(a) Absolute melting temperature of the low-melting constituent.

Thermal Expansion

After measurement of thermal conductivity of the specimens described in Table 8 and shown in Figure 21, several were used for determining the mean linear-thermal-expansion coefficients.

Method and Apparatus

Linear-thermal-expansion measurements were made in a vertical quartz-tube recording dilatometer with the specimen protected by a vacuum of approximately 5×10^{-5} mm of mercury. The specimens were given two thermal cycles from room temperature to 950 C and back to room temperature at a maximum heating and cooling rate

of 3 C per min. The dilatometer draws a continuous dilation-temperature curve which shows length changes with temperature. The error of linear-thermal-expansion measurements is estimated not to exceed ± 2 per cent.

Results

Table 11 gives mean linear-thermal-expansion coefficients for the specimens. Table 12 gives mean linear-thermal-expansion coefficients for the matrix metals.

It will be noted in comparing values in Tables 11 and 12 that the stainless steel and chromium cermet appear to have essentially the thermal expansion of UO_2 , although stainless steel has a thermal expansion of approximately two times that reported for UO_2 . The measured thermal-expansion values for Specimens TC-82 and TC-105 (molybdenum-matrix cermets) are less than those for UO_2 and higher than those for molybdenum, indicating that the molybdenum is restraining expansion. The mean linear-thermal-expansion measurements do not indicate structure instability, although the linear-thermal-expansion coefficients between phases vary by a factor of 2 in some cases.

Electrical Resistivity

Electrical-resistivity measurements were made on various cermets to determine if a theoretical model of heat conduction could be developed. Specimen details are given in Table 8 and photomicrographs are shown in Figure 21.

Method and Apparatus

Electrical-resistivity measurements were made in two different apparatus, both utilizing the voltage-drop method. A direct current was passed through the specimen and voltage drops were measured over known sections of the specimen. Current flowing through the circuit was determined by measuring the voltage drop across a standard resistor in series with the specimen. Measurements were taken with the current flowing normally and reversed, and the values were averaged to minimize thermal and induced potentials. Electrical resistivity measured concurrently with thermal conductivity utilized thermocouple leads for potential probes. Resistivities, measured independently of thermal conductivity were taken in the conventional manner with the specimen in a constant-temperature zone.

The error of the resistivity measurements is estimated not to exceed ± 1 per cent, the chief error being the uncertainty of potential probe spacings.

Results

Table 13 gives the observed electrical resistivity of the UO_2 cermets. Figure 26 shows a plot of the interpolated data.

TABLE 11. MEAN LINEAR-THERMAL-EXPANSION COEFFICIENTS FOR UO₂ CERMETS

Temperature Range, C	Mean Linear Thermal-Expansion Coefficients over Temperature Ranges Shown, 10 ⁻⁶ per C																											
	TC-81 ^(a)				TC-80				TC-102				TC-103				TC-82				TC-105				TC-104			
	Second Thermal Cycle		Third Thermal Cycle		First Thermal Cycle		Second Thermal Cycle		First Thermal Cycle		Second Thermal Cycle		First Thermal Cycle		Second Thermal Cycle		First Thermal Cycle		Second Thermal Cycle		First Thermal Cycle		Second Thermal Cycle		First Thermal Cycle		Second Thermal Cycle	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
20-100	9.6	8.7	10.4	8.8	10.2	9.0	9.7	8.3	10.1	9.3	10.1	9.3	8.5	7.7	9.2	9.1	6.5	6.6	6.6	6.3	7.2	7.6	6.8	7.2	7.6	8.4	8.3	8.7
20-200	9.7	8.9	10.5	8.8	10.2	9.0	9.9	8.7	10.3	9.4	10.1	9.2	8.6	7.9	9.5	9.2	6.7	6.7	6.7	6.3	7.3	7.6	7.0	7.5	7.9	8.5	8.4	8.8
20-300	10.0	9.3	10.7	8.9	10.3	9.1	10.0	9.1	10.5	9.5	10.3	9.4	9.2	8.3	9.9	9.3	6.9	6.8	6.8	6.4	7.6	7.7	7.3	7.7	8.2	8.7	8.7	8.9
20-400	10.3	9.6	10.9	9.2	10.4	9.3	10.2	9.3	10.7	9.7	10.5	9.6	9.5	8.6	10.2	9.5	7.1	6.9	6.9	6.6	7.8	7.8	7.6	7.9	8.7	8.7	9.1	9.1
20-500	10.6	9.9	11.1	9.5	10.6	9.5	10.4	9.5	10.9	9.9	10.7	9.8	9.8	9.0	10.4	9.8	7.3	7.1	7.0	6.8	8.0	7.9	7.9	8.1	9.1	9.2	9.4	9.4
20-600	10.8	10.2	11.3	9.9	10.7	9.8	10.6	9.8	11.1	10.1	11.0	1.01	10.1	9.5	10.7	10.0	7.5	7.3	7.2	7.0	8.2	8.1	8.3	8.3	9.4	9.4	9.7	9.6
20-700	11.0	10.7	11.4	10.4	10.8	10.1	10.7	10.2	11.2	10.5	11.1	10.5	10.2	9.9	10.8	10.4	7.7	7.5	7.4	7.2	8.4	8.3	8.5	8.5	9.7	9.7	9.9	9.8
20-800	11.1	11.1	11.5	10.9	10.9	10.5	10.8	10.5	11.3	10.8	11.2	10.8	10.4	10.2	10.9	10.7	7.9	7.8	7.7	7.5	8.7	8.5	8.8	8.7	9.9	9.9	10.1	10.0
20-900	11.3	11.4	11.6	11.4	11.0	10.8	11.0	10.9	11.4	11.1	11.3	11.1	10.6	10.5	11.0	11.0	8.2	8.0	7.9	7.8	8.8	8.7	9.1	8.9	10.2	10.1	10.3	10.2
20-950	11.3	11.6	11.6	11.7	11.0	11.0	11.2	11.0	11.5	11.3	11.3	11.2	10.7	10.7	11.1	11.1	8.3	8.1	8.0	7.9	9.0	8.8	9.2	9.0	10.3	10.2	10.4	10.3

(a) Due to a malfunction in the recording dilatometer, the first thermal cycle was not used.

TABLE 12. LITERATURE VALUES FOR THE MEAN LINEAR-THERMAL-EXPANSION COEFFICIENTS OF THE MATRIX MATERIALS

Temperature Range, C	Mean Linear-Thermal-Expansion Coefficients Over the Temperature Ranges Shown, 10^{-6} per C						UO ₂ ^{(16)(c)}
	Molybdenum ^{(12)(a)}	Molybdenum ⁽¹³⁾	Chromium ⁽¹⁴⁾	Chromium ⁽¹³⁾	Niobium ^{(15)(b)}	Type 302 Stainless ⁽²¹⁾	
20-100	4.5	5.0	6.3	6.9	7.10	16.3	--
20-200	4.9	5.0	7.2	7.2	7.21	16.9	--
20-300	5.2	5.0	7.9	7.5	7.32	17.1	--
20-400	5.3	5.2	8.4	8.0	7.62	17.6	--
20-500	5.5	5.3	8.8	8.5	7.53	18.1	--
20-600	5.6	5.4	9.1	9.0	7.64	18.7	--
20-700	5.6	5.5	9.6	9.4	7.76	19.3	--
20-800	5.6	5.6	9.9	9.9	7.85	20.0	--
20-900	5.7	5.7	10.2	10.4	7.95	--	--
20-1000	5.8	5.8	10.9	10.8	--	--	10
20-1100	5.9	6.0	11.4	11.4	--	--	--
20-1200	6.1	6.1	11.8	11.9	--	--	--
20-1300	6.2	6.3	12.3	12.4	--	--	--
20-1400	6.4	6.4	12.9	13.0	--	--	--
20-1500	6.6	6.6	13.6	13.5	--	--	--
20-1600	6.8	6.7	14.0	14.1	--	--	--

(a) Superscript numbers refer to references at end of report.

(b) Coefficient from 18 C to indicated temperature.

(c) Coefficient from 0 C to indicated temperature.

TABLE 13. OBSERVED ELECTRICAL-RESISTIVITY VALUES OF UO₂ CERMET SPECIMENS

TC-81 ^(a)		TC-80 ^(a)		TC-102 ^(b)		TC-103 ^(b)		TC-82 ^(a)		TC-90 ^(a)		TC-105 ^(b)		TC-104 ^(b)		TC-115 ^(a)		TC-130 ^(a)	
Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm	Temperature, C	Electrical Resistivity, 10 ⁻³ ohm-cm
25	1.04	25	3.21	31	1.41	38	1.47	23	0.064	27	0.156	26	0.074	90	0.248	26	0.198	24	0.316
210	1.15	226	3.37	67	1.48	50	1.49	210	0.113	125	0.210	50	0.081	100	0.254	174	0.269	237	0.435
173	1.18	164	3.00	129	1.54	101	1.56	183	0.096	106	0.208	181	0.123	145	0.281	124	0.245	205	0.415
423	1.63	442	3.22	197	1.61	195	1.62	467	0.175	234	0.247	252	0.147	211	0.320	271	0.314	177	0.403
341	1.63	320	2.81	275	1.68	250	1.67	404	0.142	195	0.239	304	0.164	261	0.365	457	0.393	599	0.607
674	2.31	672	2.41	409	1.78	350	1.76	699	0.227	374	0.312	389	0.193	304	0.400			502	0.566
559	2.31	500	1.97	518	1.85	413	1.79	613	0.190	306	0.292	465	0.223	354	0.437			417	0.532
758	1.19	192	1.95	575	1.88	491	1.84	384	0.144	515	0.386	528	0.245	402	0.472			478	0.555
642	1.23	142	1.84	639	1.92	543	1.87	331	0.144	419	0.352	644	0.286	472	0.524			405	0.524
534	1.44	550	1.94	676	1.94	605	1.92	683	0.220	659	0.492	692	0.304	540	0.567			341	0.497
441	1.47			716	1.95	727	1.97	593	0.196	537	0.423	770	0.325	606	0.619			817	0.708
				799	1.97	780	1.99	625	0.210									685	0.649
				836	1.97	854	2.02	542	0.182					802	0.341	657	0.683	570	0.605
				868	1.98			350	0.117					826	0.352	710	0.714	858	0.731
								302	0.123					864	0.366	748	0.747	723	0.661
								747	0.235					800	0.794			603	0.640
								654	0.205					831	0.792			652	0.635
														748	0.755			552	0.587
																		463	0.555
																		368	0.497
																		314	0.460
																		267	0.472
																		184	0.403
																		161	0.388
																		140	0.344

(a) Electrical-resistivity determination run concurrently with thermal conductivity.

(b) Electrical-resistivity determination run independently of thermal conductivity.

FIGURE 26. ELECTRICAL RESISTIVITY OF UO₂ CERMETS

For Specimens TC-102, TC-103, TC-104, and TC-105, which were measured concurrently with the thermal conductivity and again independently, there were no significant differences in the measured values.

Figure 26 shows the range in values and the temperature variation. As shown by these data, the resistivity was very sensitive to the minor differences among specimens. Where the thermal conductivity of the cermet varied by a factor of 3, the electrical resistivity varied by a factor of almost 100. Again, as with the thermal conductivity, there was a pattern in the stainless steel and molybdenum cermet set, but the only inconsistency in the over-all view is that the resistivity of Specimen TC-104 (chromium matrix) was between those of the two niobium cermets. From the thermal-conductivity data, the resistivity value would be expected to be between the niobium and molybdenum values.

Tremendous improvements in the thermal conductivity of UO_2 have been obtained by adding small amounts of metal. The measurements have been proved accurate by a remeasurement of several specimens and by obtaining values both in heating and cooling which agreed very closely. Thermal-expansion measurements, although only a limited amount of thermal cycling was performed on each specimen, indicate structural stability and the possibility of achieving core-cladding thermal integrity by the proper selection of matrix metal and cladding material.

THEORETICAL STUDY OF CONDUCTIVITY

An attempt was made to develop a theoretical model of the best conduction in cermets of the type considered in this report. Any such theory for predicting the conductivity of a material composed of a mixture of two or more different phases must take into account the structural arrangement of the various phases as well as the conductivity of each pure phase and the relative amount of each phase present in the material. If the conductivities of the component materials are substantially different, the structure of the mixture may have a profound effect on its thermal conductivity. This is easily seen by comparing the formulas for the conduction of heat through a medium consisting of parallel layers of the component materials.

If there is a unidirectional, uniform heat flow through a two-phase material parallel with the layers, the conductivity is given by:

$$k_m = k_1 v_1 + k_2 v_2 . \quad (1)$$

For heat flow normal to the layers the conductivity is given by:

$$k_m = \left(\frac{v_1}{k_1} + \frac{v_2}{k_2} \right)^{-1} , \quad (2)$$

where in each case k_m is the mixture conductivity, k_1 and k_2 are the component conductivities, and v_1 and v_2 are the relative volumes of the components ($v_1 + v_2 = 1$). It is easily seen that if, say, $k_2 = 0$, Equation (1) gives $k_m = k_1 v_1$ and Equation (2) gives $k_m = 0$.

Equations (1) and (2) represent theoretical upper and lower bounds, respectively, for the thermal conductivity of a two-phase material, regardless of its structure. However, in most practical cases, these limits are not sufficiently close together to be used for prediction of the mixture conductivity.

Many attempts have been made in the last 100 years to develop more accurate approximations to the conductivities of mixtures. Because of the structural complexity of most mixtures, no exact theory has been developed.

The models that have been developed are usually used to predict the variation in conductivity of the mixture with a variation in the relative volumes of its components. In the present study, cermetes were made with only two proportions of the component materials. This did not give sufficient data for a significant test of the dependence of conductivity on the relative volumes of the components.

However, if any one of the theories is to be successful in predicting the variation of mixture conductivities with relative volumes, it must also be able to correlate the variation of mixture conductivity with the variation in component conductivities as the temperature changes. If each specimen is considered alone, the relative volumes and the structures are constant and the change in the conductivity of a cermet is a result only of the change in component conductivities. As shown in Figure 25 and Table 13, the thermal conductivity and electrical resistivity of each specimen were measured over a range of temperatures. The experimental data were converted to conductivities and replotted in Figures 27 through 34. These figures show the thermal and electrical conductivities of the cermetes and of UO_2 divided by the conductivity of the metallic phase of the cermet at each temperature.

If the theories are to be applicable, the relative cermet conductivities must show the same trend with temperature as the relative UO_2 conductivities.

Since the electrical conductivity of UO_2 is infinitesimal at the test temperatures, the relative electrical conductivities of the cermetes should remain constant. As can be seen in Figures 31 through 34, the relative electrical conductivities of the cermetes are constant except for Specimens TC-102 and TC-103 (stainless steel) and TC-130 (niobium). In these three cermetes, the relative conductivity increases approximately 20 per cent over the range of temperatures. This variation cannot be readily explained.

Figures 27 through 30 show the relative thermal conductivities of the cermetes. Since the relative UO_2 conductivity in each case shows a decrease with a temperature increase, the relative cermet conductivities should also decrease. This is the case only in the niobium cermet specimens although the molybdenum cermetes, Specimens TC-82 and TC-90, do not show a significant deviation. However, the remaining specimens show a substantial increase in relative conductivity with temperature instead of a decrease.

Because of these discrepancies, the present mixture conductivity theories are not considered appropriate for predicting the thermal conductivities of these cermet specimens. This is especially true at reactor operating temperatures where the cermet conductivities seem unusually high. Because of the more reasonable behavior of the electrical conductivities of the cermetes, there would be a better chance of constructing a theoretical model for correlating these electrical conductivities.

FIGURE 27. TEMPERATURE VARIATION OF THERMAL CONDUCTIVITIES OF STAINLESS STEEL CERMETS AND UO_2 DIVIDED BY STAINLESS STEEL CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 28. TEMPERATURE VARIATION OF THERMAL CONDUCTIVITIES OF MOLYBDENUM CERMETS AND UO_2 DIVIDED BY MOLYBDENUM CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 29. TEMPERATURE VARIATION OF THERMAL CONDUCTIVITIES OF NIOBIUM CERMETS AND UO_2 DIVIDED BY NIOBIUM CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 30. TEMPERATURE VARIATION OF THERMAL CONDUCTIVITIES OF CHROMIUM CERMETS AND UO_2 DIVIDED BY CHROMIUM CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 31. TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITIES OF STAINLESS STEEL CERMETS DIVIDED BY THE STAINLESS STEEL CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 32. TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITIES OF MOLYBDENUM CERMETS DIVIDED BY THE MOLYBDENUM CONDUCTIVITY AT THE SAME TEMPERATURE

FIGURE 33. TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITY OF CHROMIUM CERMETS DIVIDED BY THE CONDUCTIVITY OF CHROMIUM AT THE SAME TEMPERATURE

FIGURE 34. TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITY OF NIOBIUM CERMETS DIVIDED BY NIOBIUM CONDUCTIVITY AT THE SAME TEMPERATURE

The discrepancy between the theoretical and experimental variations of thermal conductivity with temperature could be caused by a separation of the oxide and metal phases on cooling from fabrication temperatures. The specimens were fabricated by pressure bonding at 1204 to 1288 C. Because of the difference in thermal-expansion coefficients of the two phases, it is reasonable to expect some phase separation on cooling. This would not affect the variation of the electrical conductivity with temperature since the current is carried almost entirely by the metallic phase. However, any phase separation would tend to reduce the thermal conductivity. As the specimens are heated up, the phase separation should be reduced and the thermal conductivity improved. This is in line with the observed effect.

CONCLUSIONS

The major conclusions which can be drawn from these studies are:

- (1) Cermet reactor fuel materials containing 80 volume per cent UO_2 dispersed in either chromium, molybdenum, niobium, or stainless steel can be fabricated into uniform bodies of quite high density.
- (2) Sintering was not a successful method of densifying the cermet bodies at temperatures either below or above the melting point of the metallic phase. At the higher temperatures lack of wetting of the ceramic oxide by the liquid metals prevented the interactions required for good structural development of a cermet.
- (3) Hot-pressing techniques were used quite successfully in fabricating dense cermet bodies. A "pressure-bonding" technique was most successful in that it is much more adaptable to production processes and is more versatile in preparing various shapes than is a "press-forging" technique also investigated.
- (4) The use of spherical UO_2 provided the most desirable cermet structures and with its use continuous metal matrices could be fabricated by normal blending and pressing of oxide and metal powders.
- (5) The vapor deposition of a thin metallic coating on the individual oxide particles provided a means of obtaining a continuous metallic matrix regardless of the oxide particle shape. It should also provide a means of obtaining a continuous metallic coating at the highest possible oxide loadings although this was not investigated above 81 volume per cent.
- (6) In the compression test some ductility was measured in several of the cermet materials as indicated by a 0.2 per cent offset yield strength. In practical applications this should provide for some relief of high local stresses without serious failure.
- (7) The thermal conductivity of cermet fuel materials containing only 20 volume per cent metal is quite superior to that of pure UO_2 . At temperatures of about 800 C the measured values of the various

cermets fell within a range of about 3 to 8 times greater than pure UO_2 . From the shape of the conductivity-versus-temperature curves it appears that at higher temperatures the improvement would be even greater.

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