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THORIA AND THORIA-URANIA REINFORCED BY METAL FIBERS

by

Y. Baskin and J. H. Handwerk

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Metallurgy Division

Metallurgy Program 9.2.2

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FOREWORD

This investigation was conducted by Armour Research Foundation, Chicago, Illinois, on Subcontract No. 31-109-38-528 from Argonne National Laboratory. Information contained in this report has been taken from the various monthly and annual reports submitted by Armour Research Foundation to Argonne National Laboratory. This information had limited distribution and was not available to the usual research worker; however, since it may be of widespread interest, this report was prepared for publication.

The irradiation specimens were prepared and irradiated by Argonne National Laboratory personnel. This information is included since it is pertinent to the topic of this report.

FOREWORD

This [illegible] was conducted by Armour Research Foundation [illegible] Illinois, on Subcontract No. [illegible] from [illegible] National Laboratory. Information [illegible] in this [illegible] has been taken from the various [illegible] submitted by Armour Research Foundation to Argonne [illegible] Laboratory. This information [illegible] publication and is not available to the usual [illegible] it may be [illegible] and [illegible] this report was prepared for publication.

The [illegible] specimens were [illegible] and [illegible] by [illegible] personnel. This information is included since it is pertinent to the topic of this report.

THORIA AND THORIA-URANIA REINFORCED BY METAL FIBERS

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ABSTRACT

Thoria compacts containing refractory metal fibers in quantities as low as 5 w/o showed significantly better resistance to thermal shock spalling than thoria alone. Of the metals and alloys evaluated, molybdenum and niobium gave the best results. Values are presented for room- and elevated-temperature properties of fiber-reinforced thoria. Measured properties included compressive strength, modulus of rupture, impact strength, thermal shock resistance, thermal conductivity, thermal expansion, and oxidation resistance. The widespread presence of microcracks in these compacts resulted in significantly lower strengths and elastic moduli than those of thoria. Fibers improve resistance to thermal spalling by suppressing and limiting crack propagation and by structurally reinforcing the cracked body. Room-temperature thermal conductivity of reinforced thoria is slightly higher than that of thoria, but at 1600°C it is 3 times greater. Oxidation resistance of molybdenum-reinforced thoria is best of all combinations investigated and improves with increased specimen density. However, because of the presence of microcracks, even the densest specimens are severely attacked after 24 hr in air at 1000°C.

Thoria-urania compacts reinforced with molybdenum fibers were bonded together by means of conventional brazing techniques. Irradiation of metal-reinforced thoria-urania specimens indicated that molybdenum fibers aided the heat transfer from the fuel, whereas niobium fibers reacted with the fuel and lost their effectiveness.

INTRODUCTION

The element thorium is of interest as a fertile material for nuclear reactor applications. Fuel elements containing a mixture of thoria and urania appear promising because they could be operated at higher temperatures than the metal, thus resulting in greater thermal efficiency. Thoria is also more resistant to certain corrosive environments than the metal and, fortunately, the concentration of fertile atoms is not significantly lowered. The problem of fabricating high-density thoria bodies at moderate temperatures has been resolved by the use of small amounts of CaO,[1] CaF_2,[2] and other inorganic additives. Nevertheless, thoria has found little use in high-temperature applications because it has high thermal expansivity and modulus of elasticity which, coupled with low thermal conductivity and tensile strength, results in unusually poor resistance to thermal spalling. Although attempts have been made to improve this characteristic by varying the particle size distribution of the starting materials and by adding selected oxides to the body,[2] these have met with only limited success.

The objective of this investigation has been to improve the resistance of thoria to thermal shock and stress significantly by incorporating metallic fibers in the bodies.[3] A number of suitable metals and alloys were evaluated for this purpose. The properties of the more promising composites were determined at room and elevated temperatures since such information is needed before the composites can be considered for use in specific applications.[4] Properties evaluated were compressive strength, modulus of rupture, Young's modulus, impact strength, thermal shock resistance, thermal conductivity, thermal expansion, and oxidation resistance. In addition, samples of several reinforced thoria-urania compositions were prepared for irradiation studies.

MATERIALS AND SPECIMEN PREPARATION

Prerequisites of low thermal-neutron cross section and refractoriness severely restricted the number of metals and alloys that could be considered for incorporation in thoria. A list of metals that broadly met these requirements included: (1) mild steel, (2) stainless steel, (3) molybdenum, (4) niobium, (5) zirconium, and (6) Zircaloy-2. With the exception of Zircaloy-2, which was only available in bar stock, these metals were obtained commercially as fine wires, ranging in diameter from 0.005 to 0.025 cm. Wires were cut into short lengths of from 0.3 to 1.2 cm by means of a wire cutter; thin ribbons of Zircaloy-2 were produced by machining the bar stock.

High-purity thorium oxide powder* was used throughout the study and reagent-grade calcium fluoride was employed to promote sintering. Fine (-325 mesh) molybdenum powder was used for some experiments.

Several irradiation specimens were formed from mixtures of thoria, urania, and metal fibers. The urania used in these specimens was of 2 enrichments, either 19.2% or 93.2% enriched, and was prepared by reducing

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*Lindsay Chemical Company, Code 112.

U_3O_8 to UO_2 in hydrogen at 800°C. The metal fibers incorporated in these specimens were formed by cutting small coils of either 0.013-cm-diameter molybdenum wire or 0.013-cm-diameter niobium wire. Fibers thus formed were nominally 0.3 cm long.

In the early phases of the investigation, thoria-metal fiber compacts were formed by cold pressing, followed by sintering in an inert atmosphere at 1450°C. This proved unsatisfactory, since the relatively rigid metal fibers prevented free contraction of the thoria powder. As a consequence, fired specimens were distorted and severely cracked, and had bulk densities no higher than in the green state. Hot pressing was employed to eliminate these undesirable features. Application of pressure at elevated temperature compresses the fiber network and forces the oxide powder into voids, resulting in sound, high-density compacts.

Thoria powder (containing 0.5 w/o CaF_2) and metal fibers were intimately mixed and loaded into graphite molds, which also served as susceptors in an induction furnace. Fabrication temperatures of the order of 1500°C were attained in 20 min; samples were maintained at this temperature under approximately 170 kg/sq cm until maximum densities were obtained. In general, very little oxidation of the fibers occurred during hot pressing. Negligible interaction took place between the graphite molds and either thoria or molybdenum; however, carburization of niobium was severe. Molybdenum liners and separators were employed to isolate these specimens from the mold and thus mitigate carburization.

Three oxide compositions were fabricated for irradiation specimens: 90 w/o ThO_2-10 w/o UO_2, 70 w/o ThO_2-30 w/o UO_2, and 50 w/o ThO_2-50 w/o UO_2. The urania used in the 90 w/o ThO_2-10 w/o UO_2 mixture was 93.2% enriched, whereas the urania used in the other 2 mixtures was 19.2% enriched. The oxides were mixed in small pebble mills, and increments sufficient to form one pellet were weighed; 0.7 gm of either the molybdenum or niobium fibers was added to each increment. The metal fibers were blended with the oxides and the mixture was hot pressed in graphite molds at 1500°C under 175 kg/cm^2 pressure. A few pellets without metal fibers were also formed for purposes of comparison. The pellets thus formed were 0.95 cm in diameter and approximately 0.95 cm in length, and weighed between 6.17 and 8.28 gm. Geometric densities, calculated from the pellet dimensions, ranged from 9.30 to 9.99 g/cc for the reinforced pellets and from 8.53 to 10.05 g/cc for the nonreinforced pellets. Porosities in the reinforced pellets ranged from 3.2 to 12.2%, and from 3.8 to 17.4% for the pellets without metal fibers.

Hot pressing imparted a preferred fiber orientation in the compacts normal to the mold axis, with anisotropy being most pronounced in thin specimens. Cylindrical specimens, 3.8 cm long with an L/D ratio of 2, were used for determinations of compressive strength. Disk specimens, 6.35 cm in diameter and 2.5 cm thick, in which small holes were ultrasonically drilled for thermocouples and a central heater, served for measurements of thermal conductivity. Impact resistance was measured with bar specimens 7.6 cm long with a square cross section of 1 sq cm, in accordance with ASTM specifications. Other properties were determined for rectangular specimens 7.0 cm long, 0.635 cm thick, and of varied widths. Specimen faces were ground flat and parallel.

EXPERIMENTAL PROCEDURE

The thermal shock test consisted of heating specimens to 1000°C in air followed by quenching in a mercury reservoir at room temperature. This test was very severe, because specimen heat was rapidly dissipated and there was little opportunity for an insulative envelope to form around the compact, as occurs with water or oil quenching. The extent of thermal shock-deterioration was evaluated by measuring Young's modulus after each test.

Determinations of compressive strength and moduli of rupture were made with conventional equipment. Center-point loading was employed to determine flexural strength. Impact strength was measured by means of a Tinius-Olsen Impact Machine of the Charpy-type with a capacity of 58 cm-kg. The stress-strain diagram was obtained conventionally with the aid of SR-4 strain gages.

Equipment used to measure dynamic elastic modulus, consisting of a radio-oscilloscope, oscillator, crystal pickup, frequency counter, and amplifiers, was similar to that described by Spinner.[5] Elevated-temperature measurements of Young's modulus were performed by suspending specimens in a furnace with Fiberfrax* yarn. A magnetic cutting head connected to the oscillator drove the specimen through one cord, while specimen oscillations were detected by a crystal pickup attached to the other cord. Specimen oxidation in this test was minimized by passing helium through the furnace and by using titanium sponge to react preferentially with any oxygen present. Except for specimens containing molybdenum powder, oxidation was superficial and had negligible effect on elastic modulus.

Thermal conductivity was determined by means of a radial heat flow method,[6] whereby measurement is made of a temperature drop in a stack of disks under steady-state conditions. Disks were heated in a molybdenum-wound resistance furnace employing an inert atmosphere. The radial thermal gradient was maintained across the specimens by means of the central heater. The gradient was measured in the center of

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*The Carborundum Company, Niagara Falls, New York the 15-cm stack to mitigate end effects; thermocouple holes were located approximately 2.5 cm apart.

Thermal expansion was measured optically with tandem-mounted telescopes fitted with filar micrometer eyepieces. Oxidation penetration was measured with polished specimens which were introduced in static air at 1000°C and withdrawn after varied time intervals.

RESULTS AND DISCUSSION

Preliminary Studies

Various proportions of mild steel fibers were blended with thoria powder and hot pressed at 1500°C. Numerous small metallic globules were observed as the specimens were removed from the molds, indicating that most fibers had been extruded during fabrication. Extrusion of fibers also occurred when fabrication temperature was reduced to 1400°C. Metallographic examination of sectioned specimens confirmed that little metal remained in the compacts after hot pressing at either temperature. Fabrication temperatures lower than 1400°C were not used owing to the increased difficulty of sintering the thoria.

Thus, it was apparent that although steel melts at a higher temperature than that at which thoria begins to sinter appreciably, the metal is sufficiently soft above 1400°C that application of only moderate unidirectional pressures results in its extrusion from the compacts. As might be expected from its relatively low melting point, Type 430 stainless steel fibers exhibited similar behavior. It was therefore evident that metals considerably more refractory than steel had to be utilized to avoid extrusion of fibers during hot pressing.

Compacts which originally contained steel fibers were severely spalled after a single thermal shock, as were specimens of thoria. Evidently, the transitory presence of metal had negligible beneficial effect.

Molybdenum Fiber-reinforced Thoria

Specimens containing molybdenum fibers had densities consistently exceeding 95% of the theoretical value. Owing to the high melting point of molybdenum, extrusion of fibers did not occur. Thoria grains surrounding fibers had the same appearance as thoria of equivalent density in nonreinforced specimens. No evidence of reaction between thoria and molybdenum was observed, in accordance with the findings of other investigators[7,8] who reported no reaction between the 2 materials at temperatures up to 1800°C. In addition, carburization of molybdenum fibers was negligible.

Photomicrographs of compacts containing molybdenum fibers are shown in Figures 1 and 2. Many microcracks are seen to radiate from fiber sites in the highly magnified photograph. The cracks were produced as a result of the difference in thermal expansivity between molybdenum and thoria ($6.3 \times 10^{-6}/°C$[9] and $9.7 \times 10^{-6}/°C$[10], respectively, over the temperature range from 0 to 1500°C). This difference produces severe tensile stresses in the thoria matrix upon cooling following hot pressing.

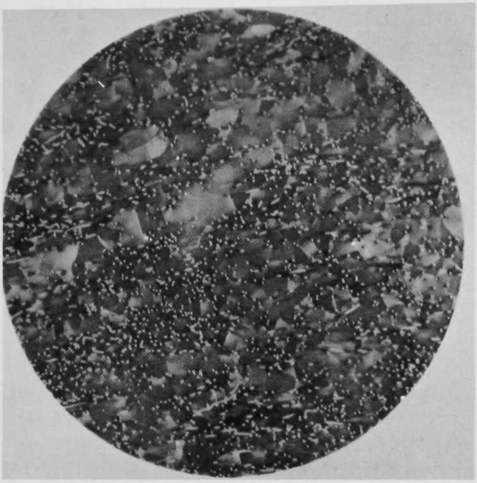

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Figure 1

Compact of Thoria Reinforced with 10 w/o of Molybdenum Fibers (0.005 cm in diameter and 0.30 cm long)

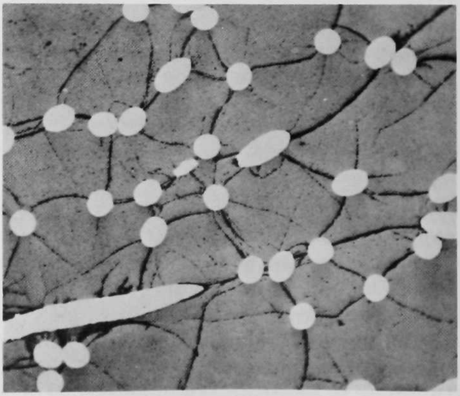

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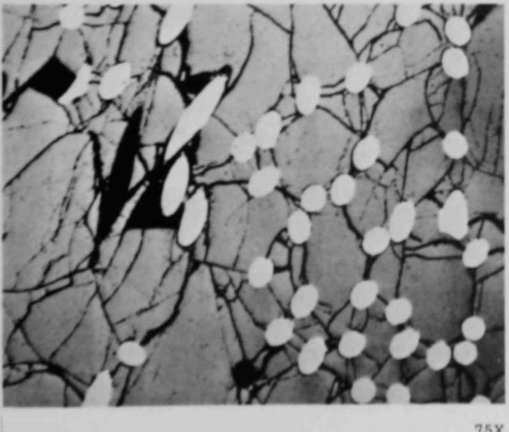
Figure 2

Same Specimen as Shown in Figure 1, but under Higher Magnification. Numerous microcracks are seen associated with the fibers.

Calculations show that these stresses exceed the tensile strength of thoria when a specimen cools below 700°C. Most stresses are relieved by the formation of numerous fine cracks, but it is likely that residual stresses are still abundant at room temperature. Most cracks are of limited extent, terminating either at intersections with fibers or other cracks. Thus, the fibers, which are responsible for development of microcracks, also confine the cracks and preserve specimen integrity. As discussed later, these characteristics profoundly affect thermal shock resistance.

In spite of the widespread presence of microcracks, or partly because of them, molybdenum fiber-reinforced thoria exhibited much better resistance to thermal spalling than thoria alone. Specimens containing only 2 or 3 volume per cent of fibers withstood 2 and 3 thermal shocks, respectively, whereas thoria was severely fractured after a single shock. The number of shocks necessary to cause failure increased with increasing fiber concentration; compacts containing 10 volume per cent of thin fibers withstood over 10 shocks. Comparing compacts with equal percentages of fibers of different diameter, those containing thin fibers showed greater resistance to spalling than those with thicker ones. This indicated that resistance improved with increasing concentration of fibers per unit volume.

A photomicrograph of a specimen subjected to 6 thermal shocks is shown in Figure 3. Cracks are more numerous and of greater width than in unshocked specimens. However, most cracks are of limited extent and still terminate either at intersections with fibers or with other cracks, thus accounting for the structural integrity of the shocked specimens. Therefore, the metal fibers improve resistance to thermal spalling by: (a) suppressing and limiting propagation of microcracks, and (b) providing a framework which maintains coherence even when the compact is severely cracked.



75X

Figure 3

Compact of Thoria Reinforced with Molybdenum Fibers Subjected to Six Thermal Shocks

Widening of cracks with thermal shock treatment is also indicated by the data in Table I. All the specimens showed diametral expansion ranging from 0.3 to 0.5% after the first thermal shock. Most specimens continued to expand after the second and third thermal shocks, but showed signs of stabilizing dimensionally after the fourth shock. Amount of speciment expansion appeared to be independent of fiber dimensions.

Table I

DIMENSIONAL CHANGE OF 10 w/o Mo FIBER-REINFORCED THORIA WITH THERMAL SHOCK TREATMENT

Fiber Diameter (cm)	Fiber Length (cm)	Specimen Diameter (cm)				
		Initial	1 Thermal Shock	2 Thermal Shocks	3 Thermal Shocks	4 Thermal Shocks
0.005	0.3	1.910	1.919	1.923	1.927	1.928
0.005	0.5	1.910	1.918	1.918	1.920	1.923
0.013	1.3	1.887	1.895	1.908	-	1.908
0.025	1.3	1.885	1.890	-	1.905	1.905

Thoria, containing up to 20 w/o of molybdenum powder, ruptured after a single shock, demonstrating that incorporation of metallic particles in these proportions does not improve resistance to spalling. The particles are not effective in stopping cracks, since cracks tend to travel between weakly bonded metallic particles, following paths of least resistance. Evidently, the increased thermal conductivity of these specimens, in comparison with thoria, had negligible effect on their susceptibility to thermal spalling.

Niobium Fiber-reinforced Thoria

Thoria grains which were darker than in nonreinforced compacts and the presence of dark diffusion halos surrounding fibers indicated that niobium and thoria interacted during hot pressing. Photomicrographs of the compacts also revealed the widespread existence of microcracks radiating from fiber sites (see Figure 4). These cracks developed for the same reason as those in compacts containing molybdenum fibers, namely, because the thermal expansivity of niobium ($7.9 \times 10^{-6}/°C$, for the temperature range from 18 to 1000°C)[11] is smaller than that of thoria. Cracks were not as numerous as in bodies containing molybdenum fibers, possibly because the thermal expansivity of thoria more closely matches that of niobium than molybdenum, resulting in reduced stresses. Concentration of cracks in compacts containing fibers of these 2 metals is reflected in their elastic moduli, 1.85×10^6 kg/sq cm and 1.51×10^6 kg/sq cm, for specimens containing 10 w/o of niobium and molybdenum fibers, respectively. As shown later, elastic modulus of a compact decreases with increased contration of microcracks.

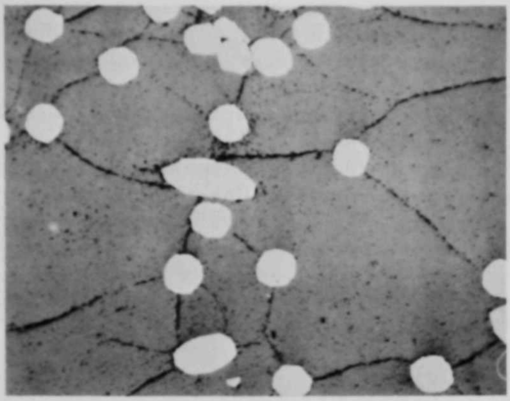


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Figure 4. Untreated Compact of Thoria Reinforced with 10 w/o of Niobium Fibers (0.007 cm in diameter and 0.5 cm long).

Compacts containing niobium fibers also withstood repeated thermal shocks without overall loss of integrity. Greatest deterioration, as shown by decreased elastic modulus, occurred after the first shock and was followed by smaller breakdown after the second. Deterioration with additional shocks was due more to oxidation of fibers than to formation of new cracks.

Thoria-niobium fiber compacts exhibited far better resistance to spalling than did thoria alone, provided the fibers did not become embrittled during hot pressing. Embrittlement is due to high-temperature reaction with carbon or the gaseous atmosphere in the graphite mold. X-ray analysis of embrittled fibers revealed that the metal had been almost completely transformed into hexagonal niobium carbide (Nb_2C). In the brittle state, fibers are not effective as crack stoppers, as cracks usually pass through such fibers and the fiber network no longer serves as an effective reinforcing agent. Niobium fibers are considerably more susceptible to carburization than fibers of molybdenum, which still possess adequate ductility after hot pressing. However, use of molybdenum liners and separators in fabrication significantly reduced carburization, and, consequently, embrittlement of niobium fibers.

Zirconium and Zircaloy-2 Fiber-reinforced Thoria

Compacts containing zirconium fibers or Zircaloy-2 ribbons possessed very poor resistance to thermal spalling. Several specimens broke in the mold upon cooling, a phenomenon which rarely occurred with pure thoria. The remaining compacts failed after a single thermal shock. Examination disclosed that the zirconium and Zircaloy-2 fibers had become highly embrittled. In contrast with embrittled niobium fibers, X-ray analysis did not reveal a carbide phase, and phases other than close-packed hexagonal zirconium were also absent. It is known, however, that zirconium becomes embrittled through contamination by relatively small amounts of either carbon or oxygen. Use of metal liners did not prevent embrittlement; presumably, the liners only isolated the specimens from the mold and there was still some access for oxygen or CO. Embrittlement might be eliminated by hot pressing in either inert atmosphere or in vacuum.

Other Ceramic and Metal Combinations

Fiber-reinforced compositions, in which up to 50 w/o of the thoria was substituted by UO_2, were successfully fabricated into dense bodies. The compacts possessed properties essentially similar to those of metal-reinforced thoria. Reinforced compacts were also fabricated with such ceramics as alumina, magnesia, zirconia, and uranium dioxide. These compositions also exhibited improved resistance to thermal spalling, compared with the pure oxides. In addition to the reinforcing metals already mentioned, Inconel, tantalum, and tungsten fibers were also evaluated. Inconel was unsuitable because of its relatively low melting point, but tantalum and tungsten proved satisfactory. Although these 2 metals have moderately high thermal-neutron cross sections, they might find use in nuclear applications where this is not a disadvantage, i.e., in fast reactors.

Other metal wire configurations besides short fibers were also evaluated and included wool and screening. These configurations might be useful in applications where a continuous metal skeleton would be desirable.

Bonding of Reinforced Compacts

Hot-pressed mixtures of oxides and metal fibers had a large number of metal fiber ends exposed on the surfaces of the compacts. These exposed fibers were firmly embedded in the oxide. Sufficient metal, however, was exposed to bond the compacts to a metal plate.

One compositon, containing 90 w/o ThO_2-10 w/o UO_2 reinforced with 10 w/o molybdenum fibers (0.015 cm in diameter and 1.90 cm in length), was brazed to a Zircaloy-2 plate. The brazing alloy used was composed of 84 w/o Zr, 8 w/o Ni, and 8 w/o Cr. This alloy is close to the ternary eutectic and has a melting point of 950°C.

Metallographic sections were made through the brazed area, and a typical structure is shown in Figure 5. The brazing alloy appears to have wet the Zircaloy-2 plate and to have reacted to some extent with the mixed oxide. In addition, the brazing alloy reacted with and dissolved some of the molybdenum. During brazing, the ceramic specimens were chipped, and the brazing alloy was found to fill the cavity formed by the chip. This demonstrated the good wetting and flow characteristics of the brazing alloy.

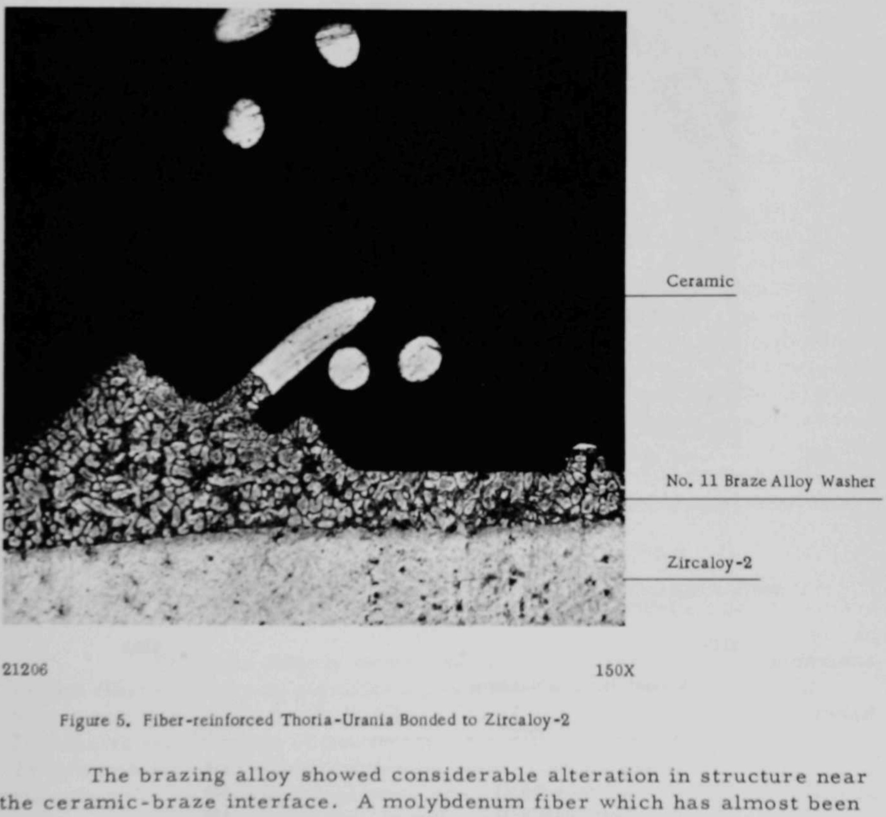

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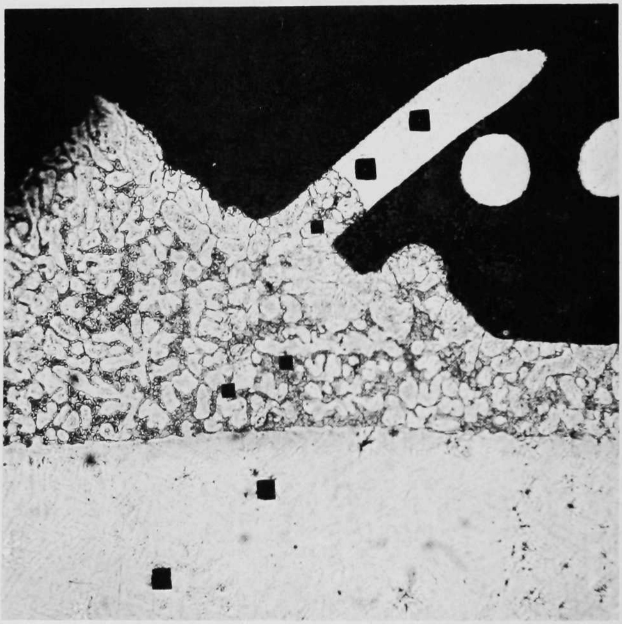
Figure 5. Fiber-reinforced Thoria-Urania Bonded to Zircaloy-2

The brazing alloy showed considerable alteration in structure near the ceramic-braze interface. A molybdenum fiber which has almost been dissolved is shown in the center of Figure 5. The brazing alloy at the junction was quite strong; however, it was rather brittle and these joints would stand very little deformation.

Hardness measurements were made on the metal fibers, before and after hot pressing, and at various locations across the braze interface. The Vicker's hardness numbers and the location of the hardness readings are shown in Figure 6. The original hardness of the molybdenum wire was measured as 225 on the Vicker's scale. After hot pressing and a slow cool to room temperature, the hardness was found to be 152. This might indicate that the molybdenum fibers were annealed during fabrication. The hardness of the molybdenum fiber after brazing (see Figure 6) was found to be 212, indicating some hardening effect due to the rapid cool following the induction heating.



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Vicker's Hardness Numbers:

Location	V.D.P.
Zircaloy-2 (Bulk)	212
Zircaloy-2 (Near Braze)	234
Braze (Near Zircaloy-2)	435
Braze (Near Molybdenum)	516
Molybdenum (Fiber after Brazing)	212
Molybdenum (Fiber after Hot Pressing, but before Brazing)	152
Molybdenum (Fiber as Received)	225

Figure 6. Locations of Hardness Measurements Made on

Property Determinations

Room-temperature Measurements

Results of the room-temperature determinations of strength and Young's modulus of fiber-reinforced thoria are presented in Table II along with published values for thoria and molybdenum. The experimental values represent an average of at least 3 determinations.

Table II

ROOM-TEMPERATURE MECHANICAL PROPERTIES

Special Composition (w/o Mo Fibers)	Fiber Diameter (cm)	Average Fiber Length (cm)	Compressive Strength (kg/sq cm)	Modulus of Rupture (kg/sq cm)	Impact Strength (cm-kg/sq cm)	Young's Modulus ($x 10^{-6}$ kg/sq cm)
ThO_2*	-	-	3,500-13,500	1,080	6.47	2.60
ThO_2**	-	-	15,500	1,060	-	2.43
Mo	-	-	6,000- 9,100	-	-	3.00
ThO_2-10 Mo Powder	-	-	N.D.†	1,320	6.38	2.63
ThO_2-2.5	0.005	0.5	N.D.	320	N.D.	1.88
ThO_2-5	0.005	0.5	3,620	230	N.D.	1.46
ThO_2-10	0.005	0.5	3,500	360	6.06	1.47
ThO_2-20	0.005	0.5	4,370	770	N.D.	1.37
ThO_2-5	0.005	1.3	N.D.	N.D.	N.D.	1.15
ThO_2-10	0.005	1.3	N.D.	460	6.28	0.89
ThO_2-20	0.005	1.3	N.D.	N.D.	N.D.	1.32
ThO_2-5	0.013	0.5	1,670	N.D.	N.D.	N.D.
ThO_2-10	0.013	0.5	2,760	270	N.D.	1.34
ThO_2-20	0.013	0.5	2,590	N.D.	N.D.	N.D.
ThO_2-10	0.013	1.3	N.D.	210	8.20	0.73

*Hot-pressed thoria. Some of the specimens used for compressive strength determinations had minute flaws, accounting for some of the low values obtained.

**Cold pressed and sintered (Lang and Knudsen)[10]

†N.D. = Not Determined.

NOTE: Values for molybdenum were taken from Materials in Design Engineering: Reference Issue of Materials Selector, p. 140 (1959).

The data clearly reveal that incorporation in thoria of molybdenum fibers results in significant reduction in compressive strength. Specimens containing 5 w/o of fibers (0.005 cm in diameter) exhibit about one-fourth the strength of thoria. Increasing the fiber concentration to 20 w/o results in stronger compacts, although still considerably weaker than thoria. Weakening by incorporation of fibers stems from the presence of numerous cracks and residual stresses in the thoria matrix. At higher fiber concentrations, this weakening is partly offset by the reinforcing influence of the fiber network. Compacts containing thicker fibers (0.013 cm in diameter) have lower compressive strengths than those with equal weight percentages of thin fibers (0.005 cm in diameter). Presumably, the reinforcing capability of a network consisting of thick fibers is lower than that of a network composed of thinner fibers, because of the much smaller number of fibers in the former case.

Values of the modulus of rupture are affected by fiber concentration and dimensions in much the same manner as are compressive strengths. Flexural strength, which is drastically reduced by the inclusion of relatively small concentrations of fibers, reaches a minimal value between 2-$\frac{1}{2}$ and 10 w/o, and markedly increases with higher fiber concentrations. Compact strength is a result of the complex interplay between the frequency of cracks and residual stresses, on the one hand, and the degree of fiber reinforcement on the other. Fiber concentration and dimensions have an important influence on both factors. Increased moduli of rupture exhibited by compacts containing molybdenum powder as compared with that of thoria indicate that the specimens are uncracked and that some sintering of metallic particles occurred.

Incorporation in thoria of thin-diameter (0.005-cm) molybdenum fibers had little effect on impact strength. Evidently, strengthening by thin metallic fibers was not sufficient to overcome the weakening effect of cracks and residual stresses on the thoria matrix. However, incorporation of thicker (0.013-cm) fibers materially enhanced resistance to impact. In line with other properties, the impact strengths of compacts containing molybdenum powder were similar to that of pure thoria.

The slight variance between the Young's modulus value for hot-pressed thoria and that reported by Lang and Knudsen[12] is attributed to differences in fabrication method and to minor compositional variations. Incorporation of fibers resulted in compacts with lower elastic moduli than thoria. Elastic modulus, paralleling flexural strength, increased with addition of molybdenum power, reflecting some metallic sintering. Apparently, the equant shapes and small size of the metal particles prevented development of stresses upon cooling.

Stress-strain determinations, performed with fiber-reinforced thoria by means of center-point loading, provided insight into the structural behavior of the material under stress. In a graphical representation of stress versus strain, the curve is linear in the elastic range and curvilinear in the plastic range. Like most ceramic substances, thoria exhibits negligible plasticity at room temperature.

A representative stress-strain diagram for fiber-reinforced thoria (see Figure 7) shows that the elastic range soon gives way to a "quasi-plastic" range resulting from the cracked condition of the compact. The presence of numerous microcracks permits small-scale structural adjustments to occur under the influence of increased stress. These adjustments become significant at moderate stress levels and are reflected in the departure from linearity of the stress-strain diagram (Figure 7), at which point the fiber network assumes increasingly greater proportions of the stress. Just prior to failure the fibers carry virtually all of the load, and specimen failure occurs when the fibers rupture and/or are pulled out of the thoria matrix.

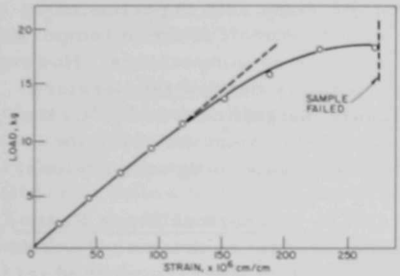

Figure 7

Stress-Strain Diagram of Thoria Reinforced with 10 w/o Mo Fibers (0.005 cm in diameter, 0.5 cm long).

Elevated-temperature Measurements

Young's Modulus - The temperature dependence of Young's modulus of thoria and thoria containing molybdenum powder is shown in Figure 8. The behavior of thoria is fairly typical of most ceramics, which exhibit a linear decrease in Young's modulus with rising temperature to about 1000°C, followed by more rapid decrease at higher temperatures. The curve for hot-pressed thoria is displaced toward slightly higher values than that reported by Wachtman and Lam,(13) but otherwise has virtually the same slope. This variance is also attributed to slightly differing physical characteristics resulting from different fabrication methods and minor compositional variation. Deviation from linearity at high temperature of the curve for thoria containing molybdenum powder was caused by oxidation of the metal, as indicated by lowered room-temperature values after testing.

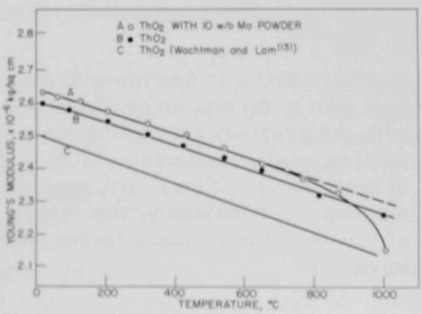

Figure 8

Young's Modulus of Thoria and Thoria with Molybdenum Powder as a Function of Temperature.

As seen in Figure 9, all fiber-reinforced specimens exhibited rising elastic moduli up to about 650°C, followed by decreases at higher temperatures. This unusual behavior contrasts sharply with that of non-reinforced specimens and appears to be related to the presence of residual stresses in the thoria matrix. On reheating to 650°C, differential thermal expansion of the 2 materials relieves many of the residual stresses, leading to an increase in Young's modulus. The increase more than offsets the normal linear reduction characteristic of thoria (see Figure 8). Relief of stresses appears to be virtually complete by 650°C, and above that temperature Young's modulus decreases at about the same rate experienced by thoria. Compacts which have the lowest elastic moduli at room temperature exhibit the greatest percentage increase with rising temperature. However, the peak values for all specimens occur in a fairly narrow temperature range. Because healing of cracks is probably insignificant at 650°C, the peak values of elastic modulus are somewhat lower than the value for thoria containing molybdenum powder at the corresponding temperature.

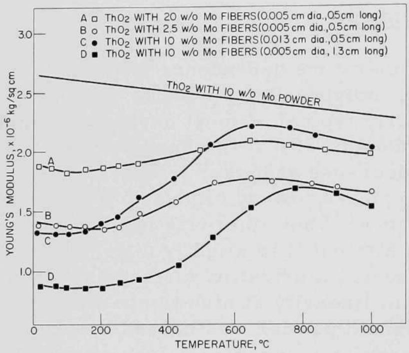

Figure 9

Young's Modulus of Reinforced Thoria as a Function of Temperature.

<u>Thermal Shock Resistance</u> - Extent of thermal shock deterioration of fiber-reinforced thoria was evaluated from determinations of Young's modulus. Data derived from these measurements are graphically presented in Figure 10; data for thoria are not given because the specimens failed after one thermal cycle. Fiber-reinforced compacts, which initially possess numerous microcracks and have lower elastic moduli than thoria, shown considerable reduction in the value after one thermal shock, indicating that additional cracks have formed. Nevertheless, after several shocks the modulus of elasticity, unlike that of nonreinforced thoria, stabilizes at a value greater than zero. Gradual decrease with additional shocks is due more to destruction of molybdenum fibers by oxidation than to formation of additional cracks. It is noteworthy that compacts with the greatest concentration of fibers show the smallest percentage reduction in elastic modulus with thermal cycling. Samples containing 20 w/o of molybdenum fibers still possess significant structural integrity after 6 shocks. Undoubtedly, the reinforcement provided by this large proportion of fibers is the primary factor responsible for the relatively high degree of integrity.

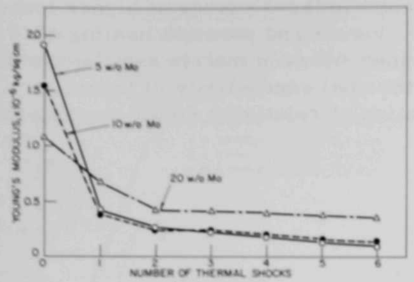

Figure 10

Effect of Thermal Shocks on Young's Modulus of Reinforced Thoria.

Modulus of Rupture - Paralleling Young's modulus, the moduli of rupture of most fiber-reinforced compacts tested are higher at 650°C than at room temperature (see Table III), a fact that mainly results from relief of stresses. Failure of compacts containing 20 w/o of molybdenum fibers to follow this trend is not understood, particularly in view of the Young's modulus behavior of this composition (see Figure 7). Compacts containing the longer and thicker fibers show the greatest percentage increase in flexural strength at 650°C, compared with room-temperature values.

Table III

MODULUS OF RUPTURE

Specimen Composition (w/o Mo Fibers)	Fiber Diameter (cm)	Fiber Length (cm)	Modulus of Rupture (kg/sq cm)	
			25°C	650°C
ThO_2 (Lang & Knudsen[10])	-	-	1060	1070
ThO_2-2.5	0.005	0.5	320	400
ThO_2-5	0.005	0.5	230	390
ThO_2-20	0.005	0.5	770	740
ThO_2-10	0.013	1.3	210	480

Thermal Conductivity - Thermal conductivity data for thoria and thoria reinforced with 10 w/o of molybdenum fibers are illustrated in Figure 11. The data show that the low-temperature thermal conductivity of fiber-reinforced thoria is only slightly higher than that of thoria, but that the difference becomes more pronounced at elevated temperature. At 1600°C, the thermal conductivity of fiber reinforced thoria is about 3 times higher than that of thoria, when, the data of Kingery *et al.*[14] is extrapolated to that temperature. Increasing divergence in the 2 curves at higher temperatures is presumed to be a result of closure and possible healing of microcracks, and improved thermal contact between matrix and fibers. It is thus seen that the high-temperature thermal conductivity of thoria is substantially improved by the incorporation of relatively small amounts of thermally conductive fibers.

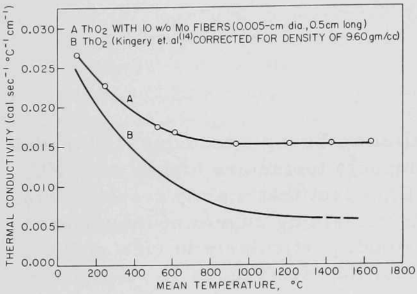

Figure 11

Thermal Conductivity of Reinforced Thoria as a Function of Temperature

Thermal Expansion - Data listed in Table IV disclose that the thermal expansion coefficient of thoria containing molybdenum powder is slightly lower than that of thoria. This is attributed to the incorporation of a lower-expansion material. Compacts containing molybdenum fibers exhibited still lower coefficients of thermal expansion because of the dissipation of some thermal expansion by closure of microcracks.

Table IV

THERMAL EXPANSION

Composition	Fiber Diameter (cm)	Fiber Length (cm)	Coefficient of Linear Expansion × 10^6 (20-1200°C)
ThO_2 (Hot Pressed)	-	-	9.76
ThO_2 (Lang & Knudsen(10))	-	-	9.62
ThO_2-10 w/o Mo Powder	-	-	9.15
ThO_2-10 w/o Mo Fibers	0.005	0.5	8.03
ThO_2-10 w/o Mo Fibers	0.005	1.3	7.85
ThO_2-10 w/o Mo Fibers	0.013	0.5	8.22
ThO_2-10 w/o Mo Fibers	0.013	1.3	8.01
Molybdenum	-	-	6.31*

*For temperature range from 20 to 1500°C.

Corrosion and Oxidation Resistance - Compacts containing 10 w/o of molybdenum of niobium fibers showed no dimensional or weight change after autoclaving at 200°C for 17 hr.

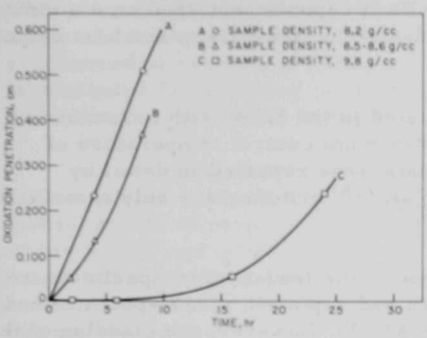

Figure 12. Oxidation Resistance of Reinforced Thoria

Results of static oxidation experiments with molybdenum fiber-reinforced thoria are shown in Figure 12. As might be anticipated, density has an important bearing on oxidation resistance; compacts with densities approaching the theoretical value show considerably greater resistance than those of lesser density. Nevertheless, even the most dense compacts are severely attacked after 24 hr of exposure to air at 1000°C. This is primarily due to the fact that diffusion of oxygen proceeds along microcracks and the essentially continuous paths of the fiber network, so that all of the metal is ultimately destroyed. The volatility of molybdenum oxide(s) and the high diffusion rate of molybdenum along grain boundaries are additional factors accelerating oxidation. Compacts become deformed and friable upon complete oxidation of the fibers.

Compacts containing niobium fibers deteriorated much faster than those incorporating molybdenum fibers. Niobium oxides are solid at 1000°C, and, since they are less dense than the metal, cause severe spalling of the matrix during formation. After an hour in air at 1000°C, these compacts are reduced to a powdery mass.

Oxidation resistance of molybdenum fiber-reinforced thoria was improved by application of flame-sprayed coatings of alumina and stabilized zirconia and by vapor deposition of molybdenum disilicide on the surface of the fibers. However, the most protective coating ($MoSi_2$) reduced, but did not stop, oxidation at 1000°C.

Irradiation Behavior - Irradiation specimens were assembled by inserting 2 ceramic pellets of the same composition in jackets formed of 0.05-cm-thick Zircaloy-2. The annulus between the fuel pellets and the jacket wall was filled with either lead or helium. The annulus for the lead-filled specimens was 0.16 cm, and in these specimens the ceramic pellets were centered by means of three 0.16-cm square, Zircaloy-2 longitudinal spacers. The annulus for the helium-filled specimens was 0.0025 cm, and in these specimens no spacers were used. End caps were heliarc-welded to all specimens to complete the assembly.

All specimens, clad and unclad, were irradiated singly in aluminum capsules containing NaK, with the space above the NaK evacuated to 0.2 μHg. The specimens were loosely held in the capsules in an annulus of stainless steel wool which prevented damage from mechanical shock and also centered the specimen in the capsule. Each capsule contained an aluminum-cobalt flux monitor which was used to determine the burnup and heat output of the specimen.

The specimens were irradiated in the ETR, with a maximum burnup of about 30,000 MWD/T and a maximum central temperature of 3200°C. Results of these irradiation tests were reported in detail by Neimark and Kittel[15] and Neimark et al.,[16] and they are only summarized in this report.

Post-irradiation examination of the lead-bonded specimens revealed that the cladding of one specimen had ruptured. This specimen had been irradiated to a burnup of 31,100 MWD/T. However, the cladding of the remaining lead-bonded specimens appeared to be unaffected by burnups as high as 29,700 MWD/T. In contrast, the cladding of most of the helium-bonded specimens showed signs of melting.

The unclad, nonreinforced pellets, when removed from the capsules, were found to be broken into many small pieces, whereas the clad reinforced pellets were broken into no more than 3 pieces and in come cases remained whole. The fracture in the reinforced pellets was usually at the midplane of the pellet and could be due to a weakness caused by the pressing method. Microstructure of random pieces of unclad, nonreinforced pellets indicated that the pieces had been irradiated at low temperatures. This was caused by the fragmentation of the pellets, which exposed a large surface to the NaK coolant.

Clad, nonreinforced pellets in which the annulus between the jacket and pellets was filled with lead exhibited a characteristic central void with large grains near the center of the pellets. In some cases, in which the cracks in the pellets were large, lead was observed to have penetrated into these fissures. Jacketed pellets which were reinforced with molybdenum fibers also showed thermal effects which resulted in the formation of a central void. The specimens with the helium-filled annulus had some metal spheres of molybdenum in the central void, and it was evident that these specimens had steeper thermal gradients than the specimens with the lead-filled annulus. Specimens with the lead-filled annulus also exhibited evidence of melting of the molybdenum fibers, for molybdenum was observed in many grain boundaries. In these specimens the central void was rather irregular, and the metal fibers appeared to be unaffected in the outer third of the pellet.

Nonreinforced ThO_2-UO_2 pellets exhibited prominent void formation and recrystallization after 15,000 MWD/T burnup at 37.7 cal/sec-sq cm. Comparable thermal effects did not occur in fiber-reinforced specimens until heat fluxes of the order of 68 cal/sec-sq cm were attained. This behavior is clearly related to the improved heat transfer characteristics of reinforced bodies. Columnar recrystallization was also less pronounced in reinforced pellets than in the pure ceramic specimens. This is accounted for by lower temperatures and thermal gradients in reinforced specimens as well as by the interfering effect of the fibers themselves.

Improvement in thermal conductivity through fiber reinforcement was also evidenced by increased thermal shock resistance. Nonreinforced pellets were severely cracked and fell apart during irradiation, whereas clad and unclad reinforced pellets showed much less tendency to crack. The crack-suppressing and reinforcing mechanisms described earlier undoubtedly played important roles in preserving specimen integrity during irradiation.

During irradiation, the niobium fibers in both clad and unclad specimens reacted with either the atmosphere in the pellet or the thoria-urania matrix, leaving only residual traces of the fibers. This type of reaction would negate the usefulness of niobium as a reinforcing material or as an effective additive for increasing the heat transfer rate of the ceramic pellets.

CONCLUSIONS

1. Hot pressing was the only feasible means for fabricating dense, fiber-reinforced thoria compacts.

2. Mild steel and Type 430 stainless steel fibers are not suitable for reinforcement owing to their relatively low melting points. During fabrication they are completely extruded from the specimens.

3. Numerous microcracks of limited extent form in molybdenum fiber-reinforced thoria on cooling, due to the higher thermal expansion coefficient of thoria. These compacts exhibit significantly better resistance to thermal spalling than thoria; initial cracks are widened and additional ones are produced as a result of thermal shock. Fibers prevent catastrophic failure by limiting crack propagation and by maintaining structural coherence even though the ceramic portion of the specimen is severely fractured.

4. Niobium fibers react with the thoria matrix during hot pressing. Compacts containing these fibers show good resistance to thermal spalling, provided the fibers do not become embrittled during fabrication. Niobium is very susceptible to embrittlement through interaction with the mold atmosphere, and precautions must be taken to minimize carbon attack.

5. Owing to embrittlement of zirconium and Zircaloy-2 during hot pressing, compacts containing these fibers show poor resistance to spalling.

6. Incorporation of fibers in thoria results in substantial reductions in compressive strength, modulus of rupture, and Young's modulus. Minima for these properties occur in the range from $2\frac{1}{2}$ to 10 w/o of metal, depending on fiber dimensions. Further increases in metal concentration generally produce stronger compacts, though still considerably weaker than those of thoria. Compacts with thicker and/or longer fibers generally exhibit lower strengths and elastic moduli than those containing equal weight percentages of short, thin fibers.

7. Molybdenum fiber-reinforced compacts show increases in Young's modulus with rising temperature up to 650°C, followed by decreases at higher temperatures. This behavior contrasts sharply with the linear decreases in Young's modulus with rising temperature exhibited by both thoria and thoria containing molybdenum powder, and reflects relief of residual stresses present in the reinforced bodies.

8. Determinations of Young's modulus reveal that reinforced compacts experience significant deterioration as a consequence of one thermal shock. The second and third shocks cause less additional deterioration, and with subsequent shocks the modulus of elasticity, unlike that of nonreinforced thoria, stabilizes at a value greater than zero.

9. Paralleling elastic modulus, flexural strength of most fiber reinforced compacts is higher at 650°C than at room temperature.

10. Room-temperature thermal conductivity of molybdenum fiber-reinforced thoria is slightly greater than that of thoria, but the difference becomes greater at elevated temperatures due to closure of cracks and improved contact between matrix and fibers. At 1600°C it is about 3 times higher than that of thoria.

11. The thermal expansion coefficient of reinforced thoria is lower than that of thoria. This is partly due to the incorporation of a lower-expansion phase, but mainly because some of the expansion is dissipated in closing the microcracks.

12. Thoria containing either molybdenum or niobium fibers possesses excellent resistance to corrosion by water at 200°C. Rate of oxidation of molybdenum fibers in thoria decreases with increasing matrix density. However, even the densest specimens are severely attacked after prolonged exposure to air at 1000°C.

13. Thoria or thoria-urania shapes reinforced with molybdenum fibers can be bonded together or to Zircaloy-2 plates by metallurgical brazing techniques.

14. Incorporation of molybdenum fibers increased the thermal conductivity of ThO_2-UO_2 pellets and permitted them to withstand significantly higher heat fluxes than nonreinforced pellets before comparable thermal effects occurred. The fibers tend to reduce central void formation, retard recrystallization, and maintain specimen integrity.

15. Niobium fibers were found to react with thoria-urania fuels during irradiation. This reaction would negate the usefulness of niobium reinforcement.

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