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DEVELOPMENT OF CERMET FUEL ELEMENTS

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TABLE OF CONTENTS

	Page
ABSTRACT	5
INTRODUCTION	5
FABRICATION STUDIES	6
Sintering.	6
Infiltration	9
Hot Press Forging	9
Cladding Techniques	11
MECHANICAL AND PHYSICAL TESTING	16
Electrical Resistivity	16
Modulus of Rupture	17
Resistance to Thermal Shock	17
SUMMARY	17
FUTURE WORK	18
REFERENCES	18

DEVELOPMENT OF CERMET FUEL ELEMENTS

Stan J. Paprocki, Donald L. Keller, George W. Cunningham, and Donald E. Kizer

Fabrication techniques for making metal-ceramic fuel elements containing 60 to 90 volume per cent of UN or UO_2 in a Type 302B stainless steel matrix was investigated. A hot press-forging procedure was most successful for fabricating fuel cores with a density of 90 per cent of theoretical or better. This procedure consisted of sealing the cold-pressed core compacts in stainless steel picture-frame packs, heating to 1900 F, and pressing to a total reduction in thickness of 35 per cent. A pressure of approximately 50 tsi was used.

Specimens produced by this method were evaluated on the basis of their microstructure, modulus of rupture, electrical conductivity, and resistance to thermal shock. Microscopic and macroscopic examination showed the presence of a continuous metal skeleton even in specimens containing 90 volume per cent fuel. The modulus of rupture at room temperature varied from 22,500 psi for a specimen containing 63 volume per cent UO_2 to 9,200 psi for a specimen containing 87 volume per cent UO_2 . Both the electrical conductivity and resistance to thermal shock of UO_2 were improved by the addition of a small volume of metal.

Gas-pressure-bonding techniques appear promising for cladding these cores into composite elements.

INTRODUCTION

Three important factors that must be considered in the development of fuel elements of dense ceramic materials are (1) low thermal-shock resistance, (2) poor thermal conductivity, and (3) low strength. All of these factors may be partially improved by dispersing the ceramic fuel in a continuous metallic matrix.

The evaluation of several methods of fabricating fuel elements containing ceramic fuel material in the range of 60 to 90 volume per cent was completed. Most of the work was conducted with UO_2 dispersed in a Type 302B stainless steel matrix; however, some work was carried out with UN dispersed in stainless steel. Compounds such as UN and UC offer the advantage of an increased amount of uranium per unit volume when compared with UO_2 .

In this study the primary effort was directed toward the evaluation and development of fabrication techniques, although a limited number of mechanical and physical tests were run. Data were collected on the modulus of rupture, resistance to thermal shock, and electrical resistivity. Since hot pressing appeared to be the most feasible method of consistently producing cores having a density 90 per cent or better of theoretical, all mechanical-test specimens were produced by this technique.

The gas-pressure-bonding technique was investigated as a means of cladding fabricated cores.

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FABRICATION STUDIES

Several types of fuel and matrix materials have been considered for producing cermet fuel elements, including UO_2 , UC, and UN, in matrices of stainless steel, molybdenum, or niobium. Because many of the same problems arise in the fabrication of each of these combinations, most of the preliminary work was conducted with Mallinckrodt Hi-Fired UO_2 and Charles Hardy Type 302B prealloyed stainless steel powder. The powder-metallurgy methods of cold pressing followed by sintering, infiltration, or hot pressing were investigated.

Sintering

While sintering at 2200 F in a dry-hydrogen atmosphere did not prove to be a satisfactory method for producing UO_2 -stainless steel cermets, the results are of interest from the standpoint of developing sintering techniques for systems not considered in the preliminary work.

The most satisfactory procedure developed for mixing the materials prior to pressing consisted of blending the powders for 2 hr, adding less than 1/2 w/o ethylene glycol, and mixing an additional 2 hr. A twin-shell V-type mixer was used for all blending operations. The ethylene glycol served both as a dispersant and as a binder. Specimens were generally compacted at 30 tsi. As shown in Figure 1, at pressures above 30 tsi, a large increase in compacting pressure resulted in very little increase in density.

In general, the density of UO_2 -stainless steel powder compacts decreases upon sintering at temperatures of 2200 F. This result cannot be readily explained. Two mechanisms have been proposed in the literature. Scott and Williams⁽¹⁾ have suggested that this decrease in density during sintering occurs because the UO_2 shrinks to a greater extent than the metal, resulting in void spaces at the metal-oxide interfaces. However, in the present work, the decrease in density was due both to a decrease in weight and an increase in size. Another suggested explanation⁽²⁾, that metal oxides form from excess oxygen contained in nonstoichiometric UO_2 , was also not supported in the present work, since no metal oxide was detected metallographically in sintered specimens. In general, the specimens consisted of a continuous skeleton of stainless steel containing loosely bonded UO_2 particles, as shown in Figure 2. Although not studied in detail, a possible explanation for the decrease in density can be based on the fact that little or no sintering of the UO_2 occurs at the stainless steel sintering temperature of 2200 F. Furthermore, it appears likely that, due to the rapid heating during the sintering operation, the UO_2 both expands and cracks into smaller particles, thus creating more void space and forcing the stainless steel skeleton to enlarge in spite of the natural tendency to shrink upon sintering.

Regardless of the explanation, sintering of UO_2 -stainless steel cermets is not considered feasible since the UO_2 does not sinter to a high density and the void space between the UO_2 particles is not decreased. Consequently, the total UO_2 loading is dependent upon the maximum packing that can be attained by cold pressing. Although calculations show that loadings of up to 88 volume per cent UO_2 are possible by

FIGURE 1. EFFECT OF COMPACTING PRESSURE ON DENSITY AND THE RELATIONSHIP BETWEEN GREEN AND SINTERED DENSITY OF UO_2 -STAINLESS STEEL CERMETS

Compacts sintered 1-1/2 hr at 2200 F in hydrogen. UO_2 content is 74 volume per cent.

100X

As Polished

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FIGURE 2. STAINLESS STEEL- UO_2 CERMET SPECIMEN AFTER SINTERING

This specimen contains 74 volume per cent minus 100 plus 140-mesh UO_2 compacted at 60 tsi with minus 200-mesh Type 302B stainless steel and sintered 1-1/2 hr at 2200 F in hydrogen.

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arranging spherical UO_2 particles of two different sizes in a close-packed arrangement, cold compaction of powder commercially available has not resulted in more than 75 per cent of the space being filled with UO_2 . A second complication in the sintering process is the lack of bonding between the UO_2 and the stainless steel. Even in a 75 volume per cent UO_2 compact, full density cannot be realized by sintering.

On the other hand, sintering appears to be feasible in the niobium- UO_2 or molybdenum- UO_2 systems because sintering can be carried out at temperatures high enough to sinter the UO_2 .

Infiltration

Additions of molten metal to ceramic compacts by infiltration of the metal to form cermet structures, or the sintering of cermets above the melting point of the metal, appears promising as a method of obtaining dense structures. The procedure is not feasible for standard UO_2 -stainless steel cermets because the stainless steel does not wet the UO_2 . Nevertheless, the use of metals that do wet the UO_2 , or the addition of small amounts of compounds that will cause the metal to wet the UO_2 , should allow the use of infiltration methods.

Hot Press Forging

The hot-press-forging technique was the only method investigated that could be used to consistently produce cores of at least 90 per cent of theoretical density. The hot-pressing technique is also applicable to many systems that are not compatible at sintering temperatures. Both ceramics and metals can be hot pressed to a high density at temperatures considerably lower than those required for sintering. For example, in this work UO_2 was warm pressed to 95 per cent of theoretical density at 1900 F - a temperature at which stainless steel may be readily pressed to 95 per cent dense structures.

The same blending and compacting procedures used for the sintered specimens were used for preparing the cold-pressed compacts except that Ceremul C rather than ethylene glycol was used as a binder. Stainless steel and UO_2 powders of several particle sizes were studied.

Green compacts were degassed at 600 F in a vacuum to remove the binder and residual gases, placed in stainless steel picture-frame packs, and sealed by welding on cover plates. The cover plates were coated with MgO to aid the removal of the compacts after hot pressing. All welding was done in an argon atmosphere. The packs were press forged at temperatures of 1800 to 2100 F. A 30 to 35 per cent reduction in thickness was given to all packs at a pressure of approximately 50 tsi.

The effect of varying the UO_2 particle size in a stainless steel matrix specimen is shown in Figure 3. Metallographic examination of the hot-pressed compacts showed that the best structure was obtained when minus 200 plus 270-mesh UO_2 was used. If

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100X

As Polished

RM9437

Minus 200-Mesh Type 302B Stainless Steel
M Minus 100-Plus 140-Mesh UO_2 Hot Press
Forged at 1800 F

100X

As Polished

RM9443

Minus 200-Mesh Type 302B Stainless
Steel Minus 200 Plus 270-Mesh UO_2
Hot Press Forged at 1800 F

100X

As Polished

RM9439

Minus 200-Mesh Type 302B Stainless Steel
Minus 270 Plus 325-Mesh UO_2 Hot Press
Forged at 1800 F

100X

As Polished

RM9441

Minus 325-Mesh Type 302B Stainless Steel
Minus 325-Mesh UO_2 Hot Press
Forged at 1800 F

FIGURE 3. EFFECT OF VARYING THE UO_2 PARTICLE SIZE IN CERMET SPECIMENS CONTAINING 74 VOLUME PER CENT UO_2

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larger size UO_2 particles were used, severe fracturing occurred during hot pressing. Smaller UO_2 particles had a tendency to bridge during compaction and resulted in increased porosity. The mechanism of the warm compacting of UO_2 is not fully understood⁽²⁾, but a sintering or self-diffusion mechanism at these temperatures does not appear likely. It appears that densification is mainly dependent upon compacting the UO_2 in the cores to a high density and surrounding it with a continuous steel skeleton. Little or no difference could be noted in the structure when minus 200-mesh stainless steel was used rather than minus 325 mesh.

Hot-pressing temperatures of 1800 to 1900 F were found to give the most desirable structure. As shown in Figure 4, when higher temperatures were used more fracturing of the UO_2 occurred. Since the same total load was used at all pressing temperatures, the stainless steel, more plastic at the higher temperatures, apparently was extruded from between the UO_2 particles and pressure was applied directly to the UO_2 , causing fracture.

The effect of UO_2 loading on the microstructure is shown in Figure 5. In specimens containing up to 60 volume per cent UO_2 , the UO_2 was usually present as discrete particles or agglomerates of several particles with the result that a strong, continuous stainless steel skeleton was obtained. 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.

A representative structure of the stainless steel skeleton could not be obtained from the photomicrographs; therefore, to ascertain whether continuous skeletons were being obtained, specimens were leached 24 hr in a warm 50 volume per cent nitric acid solution and examined. Density measurements made after the leaching of a 74 volume per cent UO_2 cermet showed a porosity of 76 per cent, indicating that the skeleton being examined consisted only of stainless steel. Representative microstructures are shown in Figure 6.

A limited number of UN-stainless steel cermets were also made by hot press forging and, as shown in Figure 7, they appear very promising. The UN appears to have undergone both plastic flow and sintering with the result that a dense structure was obtained. Cermets of UC-molybdenum were also successfully fabricated but were not subjected to a detailed examination. For these studies the UN and UC were prepared by a previously described process⁽³⁾.

Cladding Techniques

The gas-pressure-bonding technique appears to be a feasible method of cladding cermet cores. The microstructure of the core-cladding interface of an 80 volume per cent UO_2 -Type 302B stainless steel hot-press-forged core which was clad with Type 304 stainless steel is shown in Figure 8. A 10,000-psi gas pressure at 1900 F for a period of 3 hr was used for pressure bonding. The low density of the core before pressure bonding (85.2 per cent of theoretical), and the consequent stressing resulting from the densification induced by the high temperature and pressure used in pressure bonding, was thought to be the cause of the cracking visible in the core.

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100X

As Polished

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Hot Press Forged at 1800 F

100X

As Polished

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Hot Press Forged at 1900 F

100X

As Polished

RM8539

Hot Press Forged at 2000 F

100X

As Polished

RM8538

Hot Press Forged at 2100 F

FIGURE 4. EFFECT OF PRESSING TEMPERATURE ON THE MICROSTRUCTURE OF CERMET SPECIMENS CONTAINING 74 VOLUME PER CENT UO_2

Minus 200 plus 270-mesh UO_2 .

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63 Volume Per Cent UO_2

74 Volume Per Cent UO_2

87 Volume Per Cent UO_2

FIGURE 5. EFFECT OF UO_2 LOADING ON THE MICROSTRUCTURE OF UO_2 -TYPE 302B STAINLESS STEEL CERMETS HOT PRESS FORGED AT 1800 F

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15X

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Specimen That Contained Minus 325-Mesh UO_2

15X

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Specimen That Contained Minus 200 Plus 270-Mesh UO_2

FIGURE 6. TYPE 302B STAINLESS STEEL SKELETON OF 74 VOLUME PER CENT UO_2 CERMET HOT PRESS FORGED AT 2000 F

The UO_2 was leached out with nitric acid.

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100X

As Polished

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FIGURE 7. DISPERSION CONTAINING 80 VOLUME PER CENT UN IN TYPE 302B STAINLESS STEEL HOT PRESS FORGED AT 1800 F

Light areas are stainless steel.

100X

As Polished

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FIGURE 8. CORE-CLADDING INTERFACE OF A CERMET-TYPE SPECIMEN CONTAINING 80 VOLUME PER CENT UO_2 DISPERSED IN TYPE 302B STAINLESS STEEL AND PRESSURE BONDED WITH TYPE 304 STAINLESS STEEL

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Metallographic examinations of core-cladding interfaces indicated that grain growth from the core matrix into the cladding was suppressed due to the smearing of UO_2 over the matrix skeleton. It is believed that improved cleaning techniques would permit growth of the stainless steel across the core-cladding interface.

MECHANICAL AND PHYSICAL TESTING

Specimens were tested to determine the effect of UO_2 loading on modulus of rupture, electrical resistivity, and thermal-shock resistance. Test specimens were prepared by the hot-press-forging technique and ground to a final size of 1 by 0.200 by 0.090 in. Standard testing techniques were employed.

Electrical Resistivity

Electrical-resistivity data obtained at room temperature are shown in Table 1. As UO_2 is an electrical insulator, these data indicate that a continuous metallic network exists even at 87 volume per cent UO_2 . Such a continuous metallic structure, of course, will also enhance significantly the thermal conductivity.

TABLE 1. ELECTRICAL RESISTIVITY AND MODULUS OF RUPTURE OF UO_2 -STAINLESS STEEL CERMETS AT ROOM TEMPERATURE

UO_2 Loading, volume per cent	Density, per cent of theoretical	Electrical Resistivity, $\mu\text{ohm-cm}$	Modulus of Rupture ^(a) , psi
40	95.5	208	63,400
50	93	150	61,800
63	92	526	22,500
70	90.8	831	16,600
74	90.4	1250	16,700
80	93	1850	15,200
87	88.9	6900	9,200

(a) Calculated from bend-test data.

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Modulus of Rupture

Data for the modulus of rupture of several UO_2 -stainless steel cermets, computed from bend tests, are also given in Table 1.

The modulus-of-rupture data obtained by bend tests of hot-pressed 80 volume per cent UN-stainless steel cermets indicate that a value of 23,800 psi is obtained compared with a value of 15,200 psi for a similar UO_2 -stainless steel cermet.

Resistance to Thermal Shock

A qualitative comparison of thermal shock was made between UO_2 of 95 per cent of theoretical density and a 74 volume per cent UO_2 -stainless steel cermet of 85.4 per cent of theoretical density by heating the specimens to elevated temperatures in a hydrogen atmosphere and quenching in cold water. Cracking and spalling of the UO_2 occurred when quenched from 1600 F; however, as shown by Figure 9, no defects are visible on the cermet quenched from 2300 F.

5X

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FIGURE 9. A 74 VOLUME PER CENT UO_2 -STAINLESS STEEL CERMET QUENCHED FROM 2300 F

SUMMARY

A cermet having a low-volume continuous metallic phase appears to possess many of the characteristics needed for a fuel material. It combines some of the advantages of both conventional dispersion and ceramic fuels. It permits a high loading of a ceramic fuel phase which is known to have good radiation stability and then, by improving both the physical and mechanical properties, the cermet would appear to provide even greater stability.

Preliminary results indicate that the presence of the continuous steel matrix impairs the strength, thermal conductivity, and thermal-shock resistance of the highly loaded cermets over that of dense UO_2 . Results of the modulus-of-rupture calculations indicated that the strength of the cermets was primarily due to the cross section of the stainless steel with little or no strength contributed by the UO_2 .

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In general, the measured resistivity appears to be proportional to the volume per cent of stainless steel present with the UO_2 having little effect. In the high loadings, there was a considerable deviation in the measurements which was probably due to non-uniformity in the skeleton. However, the electrical-conductivity calculations indicated that the small percentages of metal present should increase the thermal conductivity by a factor of 2 to 3 times that of dense UO_2 .

The thermal-shock resistance of the cermets was greatly improved over that of dense UO_2 .

The gas-pressure-bonding technique appears to be a promising method for cladding the highly loaded cores into composite fuel elements and improving the density of the as-hot-pressed cores.

FUTURE WORK

Future work already planned includes the measurement of thermal conductivity of specimens prepared by the fabrication methods described in this report. At the same time, some fabrication work will be continued in an effort to improve the dispersion of the fuel material as well as the density. Such work will include the fabrication of cores which contain UN and UC and the investigation of various matrix materials such as chromium, molybdenum, nickel, and niobium.

In addition, vapor deposition of a thin metal coating on the ceramic fuel particles will be attempted in an effort to establish feasible sintering and infiltration techniques for the production of high-density cores. A more detailed study will be made on the combinations of UN, UC, and UO_2 with chromium, molybdenum, nickel, niobium, and stainless steel. Also, data from mechanical tests and thermal-shock tests will be correlated with variations in both core-fabrication and cladding techniques.

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