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by

Allison K. Smalley
William C. Riley
Winston H. Duckworth

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BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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Allison K. Smalley, William C. Riley, and Winston H. Duckworth

Using a special reactive form of high-purity alumina, claddings were applied to UO_2 particles by a tumbling technique. The clad pellets were isostatically pressed at 100,000 psi and then sintered at 2800 F in hydrogen. Crack-free spheroidal pellets ranging from 1000 to 2000 μ in diameter were produced. The dense Al_2O_3 envelopes surrounding the UO_2 particles were estimated to be 300 to 500 μ thick.

The Al_2O_3 claddings protected the UO_2 from oxidation when the pellets were heated in air for 100 hr at 1200 or 1800 F. There was no measurable release of fission products from irradiated clad particles heat treated at 1700 F in vacuum for 7 days after exposure to 6.0×10^{12} nv for 1 hr at room temperature.

Claddings of other oxides, such as BeO or MgO, probably could be applied by the same techniques used in applying the Al_2O_3 claddings.

INTRODUCTION

Graphite is particularly attractive as a matrix material for high-temperature nuclear fuel elements because of its high strength at elevated temperatures, exceedingly high melting or sublimation point, excellent resistance to rupture by thermally induced stresses, and good moderating ability. Studies have shown that sound bodies can be obtained with up to 40 w/o UO_2 dispersed in graphite. The mechanical and thermal properties are not altered appreciably by UO_2 contents up to at least 18 w/o. Further, it has been shown that relatively high exposure to radiation causes no physical disintegration of fueled graphite.

The major causes for concern about graphite as a fuel-matrix material are the possibility of undesirable radiation effects caused by attenuation of fission recoils and questionable fission-product retention.

One concept that appears to have excellent potential for solving both of these problems involves cladding UO_2 fuel particles with a dense, impervious shell of ceramic oxide. The composite granules then could be dispersed in graphite. The shell would be expected to attenuate fission recoils and prevent their diffusion into the graphite.

The ceramic oxides that are promising for this application from the standpoint of refractoriness and reasonable neutron absorption cross section include BeO, MgO, Al_2O_3 , ZrO_2 , and Y_2O_3 . All of these oxides appear to be compatible with UO_2 , and with graphite at least to moderately high temperatures. Alumina was selected for the first work in this area because of its availability and ease in handling, and because recent advances in technology have provided techniques for preparation of alumina ceramics having greatly improved structural properties.

The purpose of this report is to describe progress in fabrication and evaluation of Al_2O_3 -clad UO_2 particles.

EXPERIMENTAL WORK

Two methods of creating an envelope of densely sintered Al_2O_3 around UO_2 particles were investigated. The successful one consisted of spraying tumbling UO_2 particles with a slip containing Al_2O_3 , compacting, and then sintering the resulting pellets. The other, involving the leaching of UO_2 from the surface of particles consisting of uniform dispersions of UO_2 in Al_2O_3 , did not produce the desired envelopes, and this method will not be discussed.

Materials

The Al_2O_3 powder used in this program was a particularly reactive form developed in recent work at Battelle. Ceramics made from this powder under relatively mild sintering conditions are characterized by high purity, small crystal size, and high bulk density. As a result of these properties, the moduli of rupture of the experimental ceramics are exceptionally high, exceeding by about 35 per cent the moduli of rupture of high- Al_2O_3 ceramics made from conventional materials. Permeability measurements indicate that the sintered Al_2O_3 is impermeable to argon at room temperature.

The nuclear fuel used in these experiments was natural UO_2 , light ceramic-grade powder, supplied by Mallinckrodt Chemical Works. Microscopic examination of the as-received powder revealed that it consisted of aggregates ranging in diameter from 2 up to about 125 μ , with an average aggregate diameter of about 6 μ . The aggregates consisted of crystals with diameters ranging from 0.8 to 1.5 μ .

Fabrication of Al_2O_3 -Clad UO_2 by a Tumbling Technique

Uranium dioxide particles in the size range of minus 18 to plus 30 mesh (590 to 1000 μ) were prepared by adding 3 w/o beeswax to as-received UO_2 powder, compacting the mixture at 10,000 psi, crushing the compacts, and then screening the crushed material to provide the desired particle size. These particles were placed in a 10-in.-diameter rubber-lined drum. The drum was rotated at 30 to 40 rpm, and the tumbling UO_2 particles were sprayed with a slurry consisting of 33.5 w/o of gum arabic, 53.0 w/o of ethyl alcohol, and 13.5 w/o of H_2O . A gum arabic coating about 300 μ thick was applied in this manner to the UO_2 particles. This organic coating, which was eliminated during the early stages of the sintering operation, was necessary to provide space into which the subsequently applied Al_2O_3 cladding, which had a higher shrinkage than did the UO_2 , could shrink with little or no restraint during densification.

The tumbling gum arabic-coated UO_2 particles then were coated with Al_2O_3 by alternately spraying them with an Al_2O_3 -containing slip and sifting minus 100-mesh Al_2O_3 powder onto them. The Al_2O_3 slip was prepared by blending the following in a Waring Blender:

<u>Ingredient</u>	<u>Amount, w/o</u>
Al ₂ O ₃ powder	28.6
Carbowax 4000(a)	0.5
Goulac ^(b)	0.1
C ₂ H ₅ OH	31.3
H ₂ O	39.5

(a) Carbide and Carbon Chemicals Company.

(b) American Gum Products Company.

In this manner, spheroidal composite pellets, the bulk of which were in the size range from minus 6 to plus 12 mesh (1680 to 3360 μ), were prepared in lots of about 150 g. The Al₂O₃-UO₂ pellets then were dried at 120 F.

The Al₂O₃ claddings received only very moderate compaction during tumbling, and additional pressing was necessary in order to obtain pellets that could be sintered to dense, nonporous structures. The composite pellets were mixed with a pressing matrix consisting either of powdered rubber or of minus 100 plus 200-mesh calcined Al₂O₃ powder. These powdered materials flowed readily under pressure without developing any appreciable bond. The mixture was placed in rubber sleeves, deaired, and compacted isostatically at 100,000 psi. Pressed pellets then were separated from the pressing matrix by screening.

Compacted pellets were sintered by heating for 1 hr at 2800 F in flowing hydrogen. About 8 hr was required to reach maximum temperature, and the pellets were cooled with the furnace.

Evaluation of Al₂O₃-Clad UO₂ Pellets

The sintered Al₂O₃-UO₂ pellets were spheroidal in shape and crack-free. They ranged from 1000 to 2000 μ in diameter. It was estimated that the UO₂ cores ranged from 400 to 800 μ in diameter. However, the UO₂ particles were far from spherical. Thus, the cladding thicknesses were nonuniform and could not be measured readily. A chemical analysis of one lot of pellets indicated that their average UO₂ content was 23.0 w/o.

Experience with sinterable Al₂O₃ and MCW light ceramic-grade UO₂ indicated that bulk densities of about 99 and 85 per cent of theoretical could be expected for the Al₂O₃ claddings and the UO₂ cores, respectively, when fabricated under the conditions used in making the clad pellets. A photomicrograph of a polished section of an Al₂O₃-UO₂ sintered pellet is shown in Figure 1.

Three means of evaluating the quality of the claddings were used: (1) heat treatment in air, (2) measurement of alpha-particle emission, and (3) determination of fission-product release caused by heat treatment subsequent to low-temperature low-exposure irradiation.

FIGURE 1. POLISHED SECTION OF $\text{Al}_2\text{O}_3\text{-UO}_2$ COMPOSITE PELLET

The initial means of evaluating the integrity of the Al_2O_3 claddings was to heat sintered pellets in air for up to 100 hr at 1200 and 1800 F. Cracks or open pores in the claddings would permit oxidation of the UO_2 cores. Oxidation of UO_2 to U_3O_8 is quite rapid in this temperature range, and is accompanied by an increase in volume of about 36 per cent. This expansion is sufficient to rupture sintered claddings. Pellets fabricated as described in this report were not disrupted, nor was there an increase in weight as a result of the above heat treatment. This indicated that the claddings were impervious to the partial pressure of oxygen in air at atmospheric pressure and at temperatures up to 1800 F.

A second means of evaluating the continuity of the claddings was to measure the alpha-particle emission from the sintered pellets. Measurements made in a gas-flow proportional counter indicated that, during a period of 5 min, there was no alpha-particle emission from a 2-g sample of Al_2O_3 -clad UO_2 . As the ranges of alpha particles and recoil fission fragments in Al_2O_3 are similar, estimated at about $9\ \mu$, claddings which attenuate alpha particles also would be expected to attenuate fission recoils.

The quality of the claddings was evaluated further by subjecting the composite pellets to a neutron-activation test. Irradiation was carried out in the BRR. A sample consisting of about 300 pellets (2 g) was exposed to a flux of 6.0×10^{12} nv for 1 hr at room temperature. After irradiation, the sample was placed in a quartz tube, together with an activated charcoal trap. The tube was evacuated, sealed, and then heated at 1700 F for about 7 days. After heating, the charcoal trap was immersed in liquid nitrogen, sealed, and removed from the rest of the tube. Emission from the charcoal trap as measured by gamma-ray spectrometry then was used to indicate the amount of fission gas released from the sample. Results indicated that there was no measurable release of fission gas from Al_2O_3 -clad UO_2 pellets. This test for fission-product retention was considered to be unrealistically severe, since the heat treatment after irradiation was

done in a vacuum. Under these conditions, fission gases would be much more likely to diffuse through the cladding than they would under the pressure conditions anticipated in a reactor core.

The facts that the $\text{Al}_2\text{O}_3\text{-UO}_2$ pellets withstood prolonged heating in air and that they emitted no fission fragments on heating subsequent to irradiation provided a convincing demonstration that the Al_2O_3 claddings were defect-free and of very high quality.

DISCUSSION AND RECOMMENDATIONS

As mentioned previously, the selection of alumina for this work was based largely on ease of handling and progress in development of a special sinterable powder.

The major problem remaining in the fabrication of Al_2O_3 -clad UO_2 particles involves reducing the thickness of the cladding. The low thermal conductivity and poor moderating ability of Al_2O_3 dictate the use of a minimum thickness of the material. About $12\ \mu$ of Al_2O_3 would be sufficient to attenuate recoil fission fragments. However, nothing is known regarding the thickness of densely sintered Al_2O_3 required to contain fission gases.

Little is known about radiation effects in ceramic oxides induced by fission fragments at high temperature. An exploratory program at WAPD has indicated that an intimate mixture of Al_2O_3 and UO_2 is subject to appreciable swelling.⁽¹⁾ Length changes up to 30 per cent have been noted. It is not known whether the observed swelling is a property of the particular type of Al_2O_3 used or whether it is a basic property of alumina.

The techniques used in the fabrication of impervious Al_2O_3 claddings on UO_2 particles should be easily adaptable to other oxides such as BeO , MgO , or ZrO_2 . Beryllium oxide is particularly interesting because of its moderating ability and its high thermal conductivity relative to other oxides. In addition, readily sinterable BeO powders can be prepared in the laboratory. It should be noted that with BeO , which has a high thermal conductivity and is a moderator, the thickness of the cladding should be limited only by the size of the fuel particle that can be dispersed in the graphite matrix.

The potential for satisfactory reactor operation of such clad fuel particles dispersed in graphite can be assessed only by determining performance under high-temperature high-exposure irradiation conditions. Encouraging results from the first irradiations should be followed by determination of the range of reactor conditions (temperature, burnup, flux intensity, etc.) under which the fuel element will perform successfully.

The principle of using an impervious oxide cladding on UO_2 particles also could be applied to a dispersion in a ceramic oxide matrix. If satisfactory fission-product retention could be provided by the oxide cladding, such a fuel element would have interesting possibilities for use in a reactor in which an oxidizing coolant, perhaps air or CO_2 , is advantageous.

(1) References at end.

The use of impervious oxide claddings on UO_2 lends itself well to other fuel-element geometries. It may be feasible to clad massive UO_2 with an impervious oxide. Such a geometry might meet stringent requirements imposed by many reactor concepts on amount of fuel per unit volume. Fabrication of this type of fuel element has been attempted using a UO_2 core with an Al_2O_3 cladding. Preliminary testing indicated no oxidation of the UO_2 after repeated heat treatments at 2500 F. BeO also probably could be used as a cladding for this application.

REFERENCES

- (1) Technical Progress Reports on the Pressurized Water Reactor covering the period June 24, 1957, to February 23, 1958, WAPD-MRP-69, WAPD-MRP-70, WAPD-MRP-71, and WAPD-MRP-72.

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