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**Preparation of Carbide-Type, Advanced LMFBR Fuel
Pellets for Irradiation Testing**

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PREPARATION OF CARBIDE-TYPE, ADVANCED LMFBR FUEL PELLETS FOR IRRADIATION TESTING

by

R. L. Gutierrez and R. J. Herbst

ABSTRACT

A carbothermic reduction process was established to fabricate single- and two-phase uranium-plutonium carbide fuel on a production basis. Sintering temperatures of 1550 and 1800°C were used to prepare fuel densities of 98, 87, and 81% of theoretical.

I. INTRODUCTION

Uranium-plutonium carbide fuel is being considered as a prime candidate of the Advanced Fuels Program for the fast breeder reactor (FBR). The carbide fuel has higher metal density, thermal conductivity, and superior breeding ratio properties than conventional uranium-plutonium oxide fuel. Irradiation experiments were designed to investigate chemical and physical interactions between the carbide fuel and the cladding and thermal bonding medium, the fuel swelling, the fission gas release, and the migration of fuel material and fission products as a function of burnup and irradiation conditions. For this reason, carbide fuel of different densities and phase composition is being fabricated for tests being conducted in the Energy Breeder Reactor II (EBR-II) and Fast Flux Test Facility (FFTF) reactors.

II. FUEL COMPOSITION

A. Monocarbide-Sesquicarbide Phase Composition

Advanced FBR fuel pellets are fabricated by using the carbothermic reduction process. In recent years,

the composition of the fuel is of a mixed uranium-plutonium carbide of two types. The first type is essentially single-phase (U,Pu)C and the second type is two-phase (U,Pu)C + 10 vol% M_2C_3 . The single-phase fuel was fabricated at the Los Alamos Scientific Laboratory (LASL) only as 87% of theoretical density (T.D.) using the carbothermic reduction method, whereas the two-phase fuel was fabricated as 98, 87, and 81% T.D. pellets. The single-phase fuel fabricated at LASL has $\geq 93\%$ T.D. using the arc-melting method¹ and Fass² fabricated a single-phase fuel of 93% T.D. using the carbothermic reduction method.

B. Two-Phase Fuel

The two-phase composition fuel is the predominant fuel fabricated at LASL. This amounts to approximately 95% of the carbide fuel fabricated during the past 6 years. Figure 1 illustrates the basic carbothermic reduction process used to fabricate two-phase carbide fuel through sampling and inspection. The phase composition is controlled by the amount of carbon (graphite) added to the starting

Fig. 1.
Carbothermic reduction process.

oxides. We hypothesized and subsequently corroborated, by both basic studies and production experience, that the hyperstoichiometric oxygen associated with the uranium and plutonium oxides reacted at relatively low temperatures to form CO_2 . The remaining stoichiometric oxide reacted with carbon at higher temperatures to form CO . An equation³ for forming a mixed (U,Pu)-carbide was assumed as

When we compounded the starting materials according to this equation, the production and control of hyperstoichiometric compositions containing 10 ± 5 vol% of sesquicarbide were satisfactory (Fig. 2).

Fig. 2.
Compositional control in the preparation of (U,Pu)-carbide.

The 98, 87, and 81% two-phase fuel densities were prepared by the process parameters illustrated in Figs. 3, 4, and 5. For the three densities, the parameters are identical through the vacuum reduction step. It is in the comminution (grinding) and sintering steps where the process parameters are varied to obtain the particular density desired. Of the three prepared fuel densities, the 98% dense two-phase fuel is the easiest to fabricate on a production basis. To achieve high density, a small amount of nickel is used as a sintering aid. This imparts better

Fig. 3.

Process parameters for the preparation of pelleted, high-density, two-phase (U,Pu)-carbide.

control on the density and allows the use of a shorter sintering cycle. Typically, the 98% dense fuel does not vary more than 1% from one batch to another. The 81% dense fuel exhibits a 2% density variation for several batches of fuel. The 87% dense fuel often shows a 4% density variation over several batches of fuel. Figures 6, 7, and 8 show the density variation per 10 batches of 98, 87, and 81% dense fuel. The rejection rate for fuel not meeting the density specification is <1%. However, better control of the 87% dense fuel process is being sought so that the density will not vary more than 2% on a batch-to-batch basis.

C. Single-Phase Fuel

Fabrication of a single-phase 87% dense fuel is nearly identical to two-phase fuel. The only additional step added to the carbothermic reduction process is hydrogen treatment. This stage of the operation occurs between the comminution and pressing steps (Fig. 9). The process involves

Fig. 4.

Process parameters for the preparation of pelleted, 87% dense, two-phase (U,Pu)-carbide.

spreading the carbide powder in long thin trays that are inserted into a horizontal furnace. The furnace is heated to 900°C and purified hydrogen gas flows through the furnace for 0.35 hours/g of carbide powder. The hydrogen reacts with carbon as

The hyperstoichiometric system is then reduced to a single-phase state. When this method was used, fuel pellets were fabricated that were essentially single-phase material. Both chemical and microstructural analysis data verified that the fuel contained <0.2 vol% of M_2C_3 and there was no evidence of free metal. At the end of the hydrogen treatment step, the carbide powder is very reactive and care must be taken not to expose the carbide powder to oxygen or moisture levels >10 ppm. The reactive condition of the carbide powder, the additional time for hydrogen treatment, and the additional safety

Fig. 5.

Process parameters for the preparation of pelleted, 81% dense, two-phase (U,Pu)-carbide.

measures required when working with hydrogen make the fabrication of single-phase fuel more difficult than the two-phase fuel.

III. DETERMINATION OF SESQUICARBIDE CONTENT

Determination of the amount of M_2C_3 in a hyperstoichiometric fuel was challenging because of the difficult selection of an analytical technique to determine the amount of M_2C_3 . The methods pursued were the use of chemical analysis data for equivalent carbon (C+N+O) and quantitative metallography (QM). In equivalent carbon analysis, oxygen and nitrogen are assumed atomically equivalent to carbon and can be substituted for carbon in the carbide crystal lattice structure.

Fig. 6.

Density control during the preparation of pelleted, high-density (U,Pu)-carbide.

Measurements of the M_2C_3 volume proportion by these two methods correlated well for 98% dense fuel. When QM is used, the M_2C_3 appears as large grains of uniform size in the 98% dense fuel, but in the 87 and 81% dense fuel, the M_2C_3 tends to be irregular in grain size throughout the pellet. QM tended to give M_2C_3 values that were 1 to 2 vol% lower than those values obtained by carbon equivalent analysis for the two low-density fuels. The lower QM values for the low-density fuel may be due to the porosity of the material and the smaller grain size of M_2C_3 as opposed to the high-density material. This is illustrated in Fig. 10 by photomicrographs of sintered two-phase fuel pellets. Also shown is the microstructure of a single-phase fuel pellet. Because of this, the equivalent carbon method is being used to certify the amount of M_2C_3 .

Fig. 7.

Density control during the preparation of pelleted, 87% dense (U,Pu)-carbide.

specified to be in the hyperstoichiometric fuel and QM is used as a visual crosscheck.

Analytical data from many experimental batches were plotted on a graph showing M_2C_3 vol% vs carbon equivalent. These data correlated well with the line generated by assuming a stoichiometric reaction between the metals and the equivalent carbon to produce $MC + M_2C_3$. Figure 11 shows this line curve and the one generated for U_2C_3 (the insulator pellets). Both of these curves are standard for determining the amount of second-phase material in fuel or insulator pellets.

IV. FACILITIES AND PROCESS EQUIPMENT

A. Glovebox Operation and Atmosphere

Processing is done in hermetically sealed gloveboxes that are operated at a small negative

Fig. 8.

Density control during the preparation of pelleted, 81% dense (U,Pu)-carbide.

pressure compared to the room pressure. This negative pressure range is 0.25-0.50 in. of H_2O . The oxide blend is processed in a dry air atmosphere containing 15-30 ppm of moisture. After the carbothermic reduction step, the carbide material is processed in an inert atmosphere (argon) containing ≤ 10 ppm each for oxygen, nitrogen, and moisture. The inert atmosphere is maintained by a DRI-TRAIN system, which continuously recirculates the inert gas through purifier beds that physically remove the moisture and chemically remove the oxygen and nitrogen from the gas.

B. Process Equipment

Fuel fabrication initially was limited to a 500-g batch size. This limitation was due primarily to

$\text{UO}_2 + \text{PuO}_2 + \text{C}$
 BLEND — 16 h at 25 rpm
 COMPACT — 30 tsf
 REDUCE — $\left[\begin{array}{l} P_m \text{ } 500 \mu, \text{ } 1750^\circ \text{C} \\ \sim 2 \text{ h, } P_f \text{ } 5.0 \times 10^{-5} \text{ torr} \end{array} \right.$
 GRIND — 20 min/cycle
 SIEVE — 250 mesh
 HYDROGEN TREATMENT — 900°C
 PRESS — 5 - 15 tsf
 SINTER — 1800°C , 8 h 1450°C , 2 h
 CHARACTERIZE — U, Pu, C, N, O,
 SPECTROCHEM ISOTOPIC
 DENSITY, SIZE, CHIPS &
 CRACKS, RADIOGRAPHY,
 MICROSTRUCTURE

Fig. 9.

Operations and process parameters for the preparation of pelleted, 87% dense, single-phase (U,Pu)-carbide.

having a 3-in.-diam heat zone furnace for the carbothermic reduction and sintering steps. We also used a Spex mill for comminution of the briquettes, but no automatic pressing equipment. However, new facilities and equipment are now in use. The new production line has larger furnaces, a jaw crusher and vibratory mill for comminution, and an automatic press that increase the batch size to 3000 g. Figure 12 illustrates the parameters now being used with the new equipment to fabricate 98% dense two-phase fuel pellets. This line has a 300-kg/year capacity of processed material. A second production line, with a 500-kg/year capacity, will soon be operational.

87% T.D.
ONE PHASE

87% T.D.
TWO PHASE
($\sim 10\%$ M_2C_3)

98% T.D.
TWO PHASE
($\sim 10\%$ M_2C_3)

Fig. 10.

Typical microstructures of various (U,Pu)-carbide fuel types (500X, etched).

V. PLUTONIUM AND URANIUM ENRICHMENTS

The composition for the carbide fuel is $(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}_{0.99}$. The plutonium used was either 93% ^{239}Pu or 88% ^{239}Pu . Uranium enrichments of 40, 72, and 93% ^{235}U and depleted uranium were used to prepare all three densities of fuel. We encountered no fabrication problems when the enrichment content of the fuel was varied. However, it must be noted that the M_2C_3 curve of Fig. 11 will shift in the direction of the U_2C_3 curve as the uranium enrichment decreases.

Fig. 11.

Sesquicarbide content of U-carbide and (U,Pu)-carbide inferred from carbon equivalent analysis.

VI. CONCLUSION

A production process for fabricating 98, 87, and 81% dense (U,Pu)C + 10 ± 5 vol% M_2C_3 fuel was established using the carbothermic reduction method. For the single-phase fuel, the hydrogen reduction step must be improved so that processing kilogram quantities of carbide powder does not limit the rate of the total process. However, no development effort has been made in this direction because reactor experiment designers have found that the two-phase fuel exhibits less swelling than the single-phase fuel during in-reactor performance. This finding has precluded the use of single-phase fuel for current and planned irradiation tests.

Because of the equipment available at the time, the oxide blend batch size was limited to 500 g. New facilities and equipment now in operation allow 3000-g batches with a potential production rate of

Fig. 12.

Operations and process parameters used in the current process for the production of pelleted high-density (U,Pu)-carbide fuel for irradiation testing.

300 kg of two-phase carbide fuel per year. A second production line will soon be in operation and this line will process 500 kg of two-phase carbide fuel per year.

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