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MOLYBDENUM-BASE CERMET FUEL DEVELOPMENT

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INTRODUCTION

Development of a multimegawatt (MMW) space nuclear power system requires identification and resolution of several technical feasibility issues before selecting one or more promising system concepts. Demonstration of reactor fuel fabrication technology is required for cermet-fueled reactor concepts. MMW reactor fuel development activity at Pacific Northwest Laboratory (PNL) is focused on producing a molybdenum-matrix uranium-nitride (UN) fueled cermet. This cermet is to have a high matrix density (≥95%) for high strength and high thermal conductance coupled with a high particle (UN) porosity (~25%) for retention of released fission gas at high burnup. Fabrication process development involves the use of porous TiN microspheres as surrogate fuel material until porous UN microspheres become available. Process development has been conducted in the areas of microsphere synthesis, particle sealing/coating, and high-energy-rate forming (HERF) and vacuum hot press consolidation techniques. This paper summarizes the status of these activities.

PROCESS DEVELOPMENT AND RESULTS

Microsphere Synthesis

To conduct cermet fabrication process development in the absence of suitable UN microspheres, TiN was selected as a surrogate material. Porous TiN microspheres can be synthesized by the freeze-drying process, and TiN, unlike UN, is a relatively stable compound that can be handled in air. TiN microspheres approximately 30% to 50% dense and in the 75- to 200-μm-diameter range were produced by freeze drying a mixture of TiO_2 and graphite, converting this mixture to the carbide under a vacuum, and subsequently converting the carbide to TiN in a nitrogen-hydrogen gas mixture. The simplified fabrication process flow chart, Figure 1, shows the microsphere synthesis steps as part of the overall cermet fabrication process.

Seal Coating

To ensure a matrix ligament on the outer surface of the final cermet product, it is necessary to coat the fuel particles before they are consolidated. In addition, to prevent porosity plugging and/or chemical reactions between the

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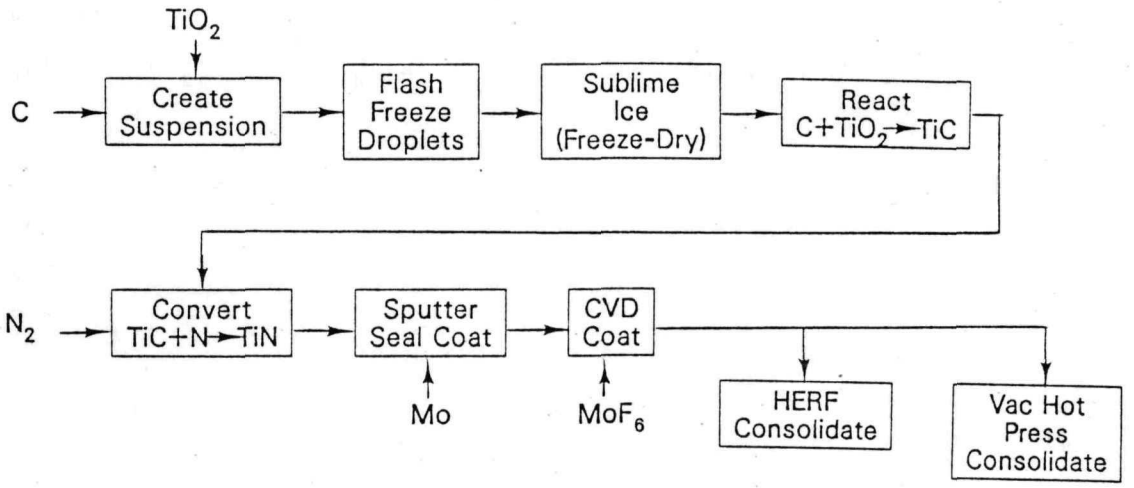

Figure 1. Simplified Fabrication Process Flow Chart

fuel particle and the process gas during the chemical vapor deposition (CVD) coating step, a seal coat of molybdenum is desirable.

Enhanced thermionically supported discharge (ETSD) high-rate sputtering was selected as the particle sealing process because of its high deposition rate capability. A coating of molybdenum greater than 10 μm thick can be deposited uniformly on 20 cm^3 of microspheres in less than eight hours and a controlled bias voltage can be applied to the microspheres during deposition to enhance sealing action.

Minor modifications were made to an existing ETSD sputter deposition system for applying the hermetic molybdenum coat to the porous TiN microspheres. A special 15.2-cm-diameter x 1-cm-deep molybdenum holding pan was prepared to contain the microspheres. The pan rotates and vibrates when excited by an adjustable external mechanical driver. This motion causes random mixing and ensures coating uniformity and sealing of porous surfaces of the microspheres during sputtering. A 15.2-cm-diameter planar molybdenum sputtering target is positioned 4.8 cm above the holding pan. The inside of the chamber is precoated with a thin film of molybdenum to prevent contamination of the microspheres during coating. After precoating, the chamber is opened, the microspheres are placed in the molybdenum pan, and the system is immediately evacuated and put on ultra-high-vacuum pumping. The chamber is then pumped overnight and typically obtains a pressure of 1.5×10^{-5} Pa (1×10^{-7} Torr) before sputter coating. The ETSD sputtering system is operated for 6.5 h at a molybdenum target removal rate of 0.45 μm/min to obtain average deposition rates of 0.025 μm/min on the microspheres. The molybdenum pan is electrically isolated to permit biasing the microspheres at -50V with respect to the grounded anode during deposition. The supported discharge is started and gradually increased over a 30-min period to its operating level to permit the TiN microspheres and the internal surfaces of the sputtering chamber to outgas as temperatures increase. (Krypton is used as the sputtering gas because it produces a higher sputtering range than argon.) Target voltage is increased to

1000V over a 5-min period. A target ion current density of 7 ma/cm^2 is maintained for the remainder of the coating run. Typically, 35 g of molybdenum are removed from the sputtering target, 50% of which is deposited onto the microspheres; the remainder is collected on reusable shields in the chamber. The temperature of the microspheres during coating is estimated at ~250°C. The ratio of coated weight to starting TiN weight is typically 2.5.

CVD Coating

CVD coating development has been performed at Battelle Columbus Laboratories (BCL). The TiN particles used to date are a surrogate for UN particles, which are being developed at Los Alamos National Laboratory (LANL). Special consideration was given to factors that later might adversely affect the integrity of UN particles at conditions normally used for molybdenum deposition. A limited number of thermodynamic free energy calculations were performed to evaluate the effect of hydrogen reduction of molybdenum halides and molybdenum carbonyl at various conditions in the presence of UN. Reasonable conditions were predicted for depositing molybdenum on UN from molybdenum hexafluoride (MoF_6) without significantly etching the UN substrate. Considerable success has been achieved with MoF_6.

Experiments to develop conditions for the deposition of molybdenum on surrogate porous fuel particles were carried out in a fluidized-bed reactor system. Deposition pressure was not found significantly to affect coating deposition, although the effect on fluidization dynamics was pronounced. Higher gas flows were found to be necessary to maintain an adequate level of fluidization at near-atmospheric pressure than were required at pressures lower than about 500 Torr. The TiN particles are fluidized for cleaning in H_2, circa 800°C, before the temperature is reduced to 600°C and a small amount (1 to 2 vol.%) of MoF_6 is introduced. A coating rate of approximately 10 μm/h is achieved under these conditions. The CVD-Mo coating tends to fill any voids or cracks in the sputtered molybdenum seal coat and otherwise to smooth the particle surface. Figure 2 illustrates sputter-seal-coated TiN particles with a CVD overlayer. If the sputtered seal coat is omitted, molybdenum is deposited in the porous structure of the TiN. This infiltration may be structurally beneficial if sufficient porosity remains to retain fission gases.

HERF Consolidation

Molybdenum-coated TiN surrogate fuels are consolidated by HERFing in a mild steel form having a tubular cavity into which the coated TiN particles are loaded. The loaded form is preheated in an evacuated stainless steel can, generally to the upper working temperature limit of the stainless steel (about 1200°C), and HERFed to consolidate the coated fuel into a dense, tubular shape. The consolidated, tubular fuel is then separated from the mild steel by machining followed by etching away the last remaining steel in hot HCl. Most of the as-HERFed strength is obtained from mechanical interlocking; subsequent heat treatment, circa 1500°C, is required to obtain diffusion bonding as well as to thermally stabilize the fuel structure for the temperatures to be experienced in reactor.

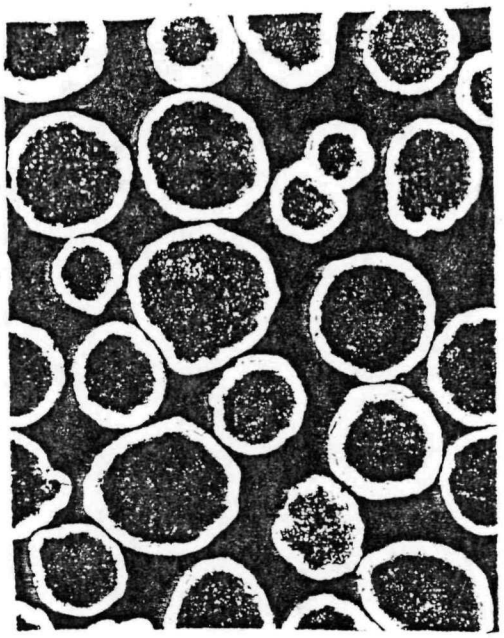

Figure 2. TiN Microspheres Coated with Both Sputtered and CVD Molybdenum Layers

Solid fuel tubes having 65 vol.% molybdenum matrix and 35 vol.% TiN have been prepared using 30% to 50% dense TiN particles that had been coated directly with molybdenum by CVD; as noted earlier, these directly CVD-coated TiN particles are infiltrated with molybdenum. There is approximately 10% residual porosity in the structure, which appears to be divided equally between the molybdenum matrix and the TiN particles. Figure 3 illustrates the coated particle interface after HERF consolidation and before stabilization heat treatment. Figure 4 shows a HERF-consolidated tube wall cross section before stabilization heat treatment. This cermet structure was subsequently heat treated for one hour at 1500°C to stabilize and diffusion bond the fuel structure. As a result, only slight densification of the cermet occurred, the molybdenum matrix recrystallized, and the residual porosity in the matrix coalesced; no significant Mo-TiN reaction was detected.

Fuel tubes have been HERFed using TiN particles that were sputter sealed before CVD coating. These TiN particles are not infiltrated with molybdenum; therefore, a higher fraction of the porosity is expected to be retained in the TiN. These cermets are currently under evaluation; it appears that the retained particle porosity is in the range from 15% to 40% depending on the original TiN particle density.

It has been found that heavy ceramic coatings (alumina or zirconia) on the mild steel form are required to prevent cracking of the fuel tube due to

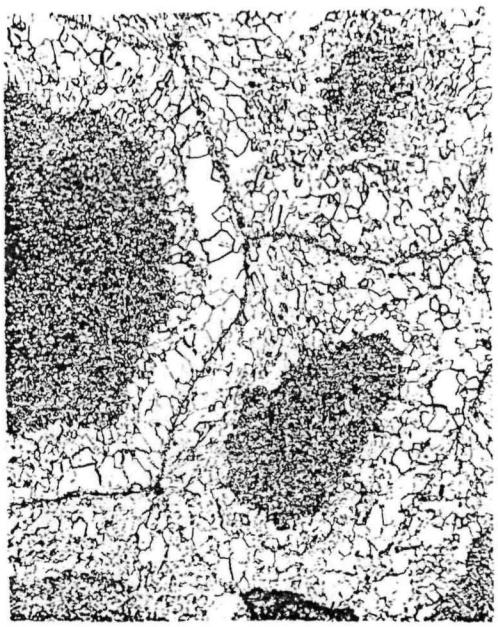

Figure 3. Coated Particle Interface After HERF Consolidation

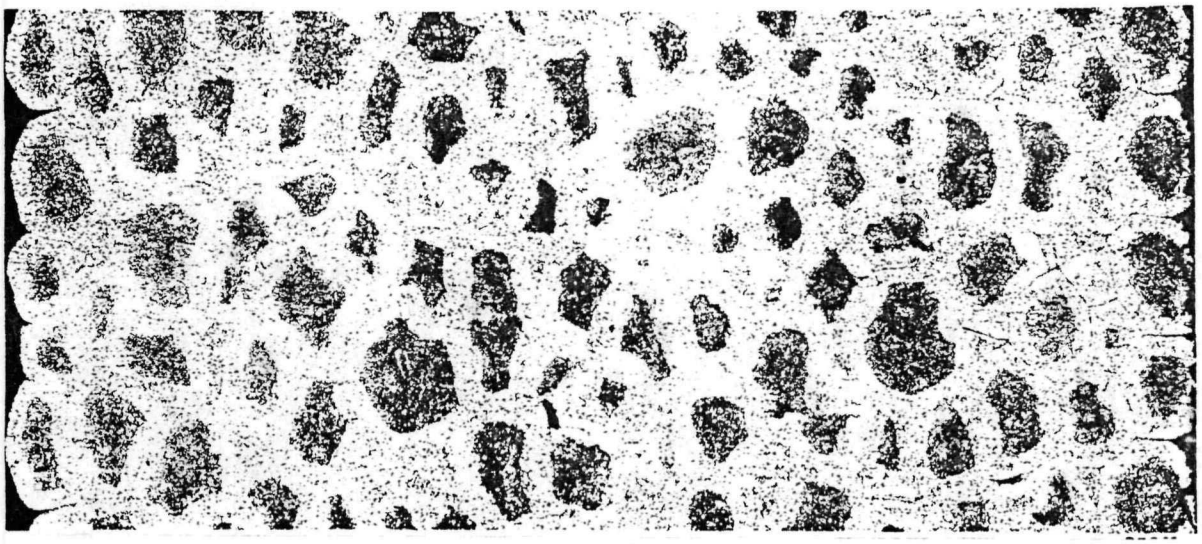

Figure 4. Cross Section of HERF-Consolidated Tube Wall Before Stabilization Heat Treatment

differential thermal contraction stresses. Compaction has been done in mild steel tooling at temperatures as low at 1000°C, but with a high incidence of fuel cracking. Attempts to use graphite forms to minimize the effect of thermal stresses have not been successful to date, chiefly because of the highly elastic behavior of graphite (as opposed to the plastic behavior of mild steel) during HERFing, which tears apart the consolidated tube. Geometry modifications are being attempted in an effort to make use of the advantages of graphite--smooth surface retention, minimization of acid dissolution of steel, and a better thermal expansion match with the consolidated fuel tube.

Hot Press Consolidation

Molybdenum-coated TiN surrogate fuels have also been consolidated by vacuum hot pressing. Two tubular specimens of CVD Mo-coated TiN have been consolidated by hot pressing. The first was pressed at 1800°C and 5000 psi. The second specimen contained 80% CVD Mo-coated microspheres and 20% molybdenum powder at pressing conditions of 1700°C and 5000 psi. Both specimens appear to have acceptable matrix densities, uneven deformation of the fuel particles due to die wall friction, and a very distinct reaction zone of molybdenum carbide where molybdenum is in contact with the graphite tooling. The molybdenum carbide reaction zone has been reduced to a near negligible thickness by adding a tantalum foil barrier between the molybdenum matrix powder and the graphite tooling wall before consolidation.

SUMMARY AND CONCLUSIONS

Development of a fabrication process for molybdenum-base TiN-surrogate fuel cermets has progressed far enough to indicate that fabricability is technically feasible. Further activities will demonstrate fabricability using depleted UN microspheres to refine and establish process variables for that system. Establishment of a fabrication process for UN is a natural progression from the work reported above.

ACKNOWLEDGMENTS

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