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An Overview of Current and Past W-UO$_2$ CERMET Fuel Fabrication Technology

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Abstract – *Studies dating back to the late 1940s performed by a number of different organizations and laboratories have established the major advantages of Nuclear Thermal Propulsion (NTP) systems, particularly for manned missions. A number of NTP projects have been initiated since this time; none have had any sustained fuel development work that appreciably contributed to fuel fabrication data from this era. As interest in these missions returns and previous space nuclear power researchers begin to retire, fuel fabrication technologies must be revisited, so that established technologies can be transferred to young researchers seamlessly and updated, more advanced processes can be deployed to develop successful NTP fuels. CERMET fuels, specifically W-UO$_2$, are of particular interest to the next generation NTP plans since these fuels have shown significant advantages over other fuel types, such as relatively high burnup, no significant failures under severe transient conditions, capability of accommodating a large fission product inventory during irradiation and compatibility with flowing hot hydrogen. Examples of previous fabrication routes involved with CERMET fuels include hot isostatic pressing (HIPing) and press and sinter, whereas newer technologies, such as spark plasma sintering, combustion synthesis and microsphere fabrication might be well suited to produce high quality, effective fuel elements. These advanced technologies may address common issues with CERMET fuels, such as grain growth, ductile to brittle transition temperature and UO$_2$ stoichiometry, more effectively than the commonly accepted 'traditional' fabrication routes. Bonding of fuel elements, especially if the fabrication process demands production of smaller element segments, must be investigated. Advanced brazing techniques and compounds are now available that could produce a higher quality bond segment with increased ease in joining. This paper will briefly address the history of CERMET fuel fabrication technology as related to the GE 710 and ANL Nuclear Rocket Programs, in addition to discussing future plans, viable alternatives and preliminary investigations for W-UO$_2$ CERMET fuel fabrication. The intention of the talk is to provide the brief history and tie in an overview of current programs and investigations as related to NTP based W-UO$_2$ CERMET fuel fabrication, and hopefully peak interest in advanced fuel fabrication technologies.*

I. INTRODUCTION

Studies dating back to the late 1940s performed by a number of different commercial organizations, national laboratories and universities have established the major advantages of Nuclear Thermal Propulsion (NTP) systems, particularly for manned missions. NTP systems are inherently superior to chemical propulsion systems because of the increased energy potential per unit mass of nuclear fuel, and the fact that use of hydrogen coolant / propellant helps attain high exhaust velocities relative to that achievable by the higher molecular weight combustion products characteristic of chemical systems. Examples of specific advantages of NTP systems as demonstrated by previous analysis include, but are not limited to:

- Reduced transit times for extended duration missions with the same initial mass to low earth orbit (IMLEO) that effectively minimize crew exposure to galactic cosmic rays, solar flares and zero gravity
- Reduced round trip transit times for short stay missions with the same IMLEO.
- Reduced IMLEO requirements for the same mission duration

- Allowance for increased mission flexibility including increased Earth and Mars departure windows, along with greater propulsion margins available for mission aborts.

Nuclear Thermal Propulsion (NTP) systems are typically characterized by very high temperature (T_{ex} ~2550-2900 K) exhaust gas, high specific impulses (I_{sp} ~875-950 sec) and relatively short operating times (~2-4 hours). Survivability under these extreme temperature and harsh environmental conditions for the design lifetime of fuel must be effectively demonstrated, and is a direct correlation to the manner in which fuel is fabricated. Specifically, the fuel must retain adequate mechanical strength and geometric integrity as well as have a suitable tolerance to high radiation fluxes and fluences present in the reactor. The fuel must be capable of retaining a high percentage of fission products during fuel lifetime and for multiple transient reactor conditions (approximately 6 cycle lifetime).

The NTP program officially began in 1955 at the Los Alamos Science Laboratory (LASL, now LANL) and Livermore Research Laboratory (LRL, now LLNL) with consideration of two fuel types: graphite based fuels (e.g. UC_2 in C) and refractory alloy based fuels (e.g. UO_2 in W or W-Re). One of the initial technical questions arising from this program was the choice of fuels, since it was clear that this would be the most complex technology choice. CERMET fuels have a relatively small, but positive, history and database in comparison to graphite based fuel forms. The CERMET fuel concept was developed practically during two significant, separate programs undertaken in the 1960s within the United States: 1) the GE-710 program that was a follow up to the Aircraft Nuclear Propulsion (ANP) program, and 2) the ANL CERMET Nuclear Rocket program that was undertaken as an alternative to the mainline carbide fueled NERVA/ROVER program. During these programs, significant contributions to prove the feasibility of CERMET fuels for NTP applications were made. Some examples of these contributions include irradiation to relatively high burnups and exposure to severe transient conditions without significant failures, demonstrated capability to accommodate a large fission product inventory during irradiation, and compatibility with flowing hot hydrogen. CERMET fuels offer the inherent intrinsic spectral shift safety feature that ensures subcriticality under both water and dry sand submersion accidents. Excellent reviews of the entire NTP fuel campaigns and concepts can be found in Refs. 1 and 2.

Only small efforts have been made regarding CERMET fuel fabrication since these two programs. Of these, efforts have been mainly directed towards re-capture of existing fuel fabrication technologies, i.e. cold press and sinter or HIP with established fuel and process parameters, and building upon the existing CERMET fuel database. There is a mounting concern that, with the rapid disappearance of researchers and operations facilities associated with the research and development of NTP CERMET fuels, over forty years of experience will be lost and irretrievable by future researchers. Most of the key assessments were never published and/or presented, and therefore can only be passed down through hands on involvement and conversation, and those assessments that are easily accessible rarely discuss specifics associated with fuel fabrication. In addition, technology has evolved significantly over the past forty years. Improved methods to fabricate CERMETs and ceramic fuels have been established that are practical for NTP fuel fabrication, and may even minimize or solve the challenges faced during the GE 710 and ANL programs. Establishing a firm foundation of the results from these programs, along with some novel, proposed ideas for CERMET fuel fabrication is necessary and in order. The purpose of this paper is to begin laying this foundation, hopefully initiating interest in young researchers so that current knowledge can be transferred seamlessly, and that new efforts can be based upon this foundation.

II. GE 710 HIGH-TEMPERATURE GAS REACTOR PROGRAM

The GE 710 High Temperature Gas Reactor (HTGR) Program sought to develop a refractory-metal-clad W-UO_2 matrix type fuel element for both NEP and NTP applications, resulting in four different program objectives.[3] Effectively, the program was in existence from 1962 until 1968 and accomplished a flexible, basic fuel element design, assessed a fabrication process and evaluated the performance objectives through both non-nuclear and in-pile testing. Major achievements during the GE 710 HTGR Program included down selection to either W-UO_2 or Mo-UO_2 CERMETs, significant development of fabrication and brazing techniques for these elements, development of sintering methods for fabrication of high-density fueled CERMETs, and initiation of in-pile testing. A consistent fuel loading of 46 wt% UO_2 was used throughout the program.

II.A. Fuel Fabrication

Factors affecting sinterability of W-UO_2 CERMETs were investigated during the first objective of the program. Initially, crucibles containing pressed elements were stacked inside the sintering furnace and subjected to the sintering conditions. This led to sintered elements with less than desirable densities and significant variations in sintered density between the bottom compact and the top compact (65-80% theoretical). Vent holes were added to the bottom of the covered sintering crucibles to allow flow of hydrogen gas past all the compacts, so that variations in density between stacked compacts was minimized, raising sintered densities to 90% theoretical or better, shown graphically in Fig. 1. In addition, tungsten powder composed of 1-2 μm diameter particles with a uniform spherical shape resulted in increased sintered densities, e.g. 95% theoretical, rather than coarser particles with a predominately angular or planar shape that created bridges during cold pressing and effectively reduced the number of contact points between particles. Typical sintering temperatures ranged from 2472 to 2672 K, with higher sintering temperatures (O/U ratio of 1.96 to 1.97) resulting in cladding leaks during thermal cycling tests while the lower sintering temperatures (O/U ratio of 1.98) did not produce a significant number of cladding leaks during thermal cycling.

Dissociation of UO_2 into free uranium metal and hyperstoichiometric UO_2 or oxygen gas had detrimental effects on fuel fabrication and selection. An increase in excess oxygen within the fuel led to an increase in swelling of the fuel element and therefore a loss in the dimensional stability, shown graphically in Fig. 2. The excess oxygen could also react with the tungsten matrix forming WO_2 stringers in the matrix grain boundaries. The decrease in dimensional stability resulted from an increase in the ductile-to-brittle transition temperature (DBTT) of the tungsten matrix by further dissociation of gaseous tungsten oxide (WO_3) as the temperature was raised above 1589 K.[4,5] Similarly, free uranium was observed to be detrimental to fuel stability, in addition to negative reactions with the cladding materials of interest. At lower temperatures, the amount of free uranium present within the tungsten matrix was observed to increase. However, there was little to no mobility of the free uranium at temperatures below the melting point. Once the temperature was elevated above the melting point (1422-1644 K), the free uranium formed a two phase mixture that resulted in fuel swelling. The challenges associated with dissociation of UO_2, in particular with free uranium metal, were first addressed by addition of a stabilizing compound, ThO_2. Thoria addition to the UO_2 agglomerates was believed to restrain and/or retard channeling of free uranium into the matrix metal and eventually into the cladding. However, this was not observed to be the case. Addition of ThO_2 only delayed free uranium migration, but did not entirely retard the mobility. The more suitable solution to UO_2 dissociation was the use of substoichiometric UO_2 combined with the ThO_2 stabilizer. Substoichiometric UO_2 was found to retain a single phase while at temperature. Dissociation and free uranium migration became an issue only during thermal cycling, and was believed to be corrected by using a cladding material not susceptible to uranium metal attack. Oxygen to uranium ratios varied from 1.96 to 1.98, with a value between 1.984 and 1.988 being the best performer during thermal cycling tests.[6] Post sinter heat treatments of fueled cores in a H_2O- saturated hydrogen environment was initially believed to minimize the extent of cladding leakage resulting from oxidation of free uranium formed from dissociation during sintering. This treatment was abandoned in the latter program objectives because the wet-dry H_2 treatment with approximately 12 ppb H_2O was found to be excessive for UO_{2-x} oxidation and detrimental to overall fuel element performance.[7-9]

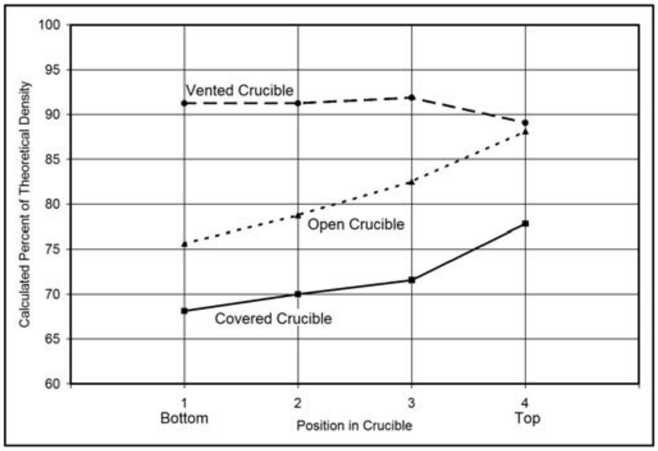

Fig. 1. Effect of hydrogen gas accessibility on calculated percent of theoretical sintered density as a function of crucible position. Compacts were sintered in both open and covered crucibles for one hour in hydrogen at 2673 K, while compacts were sintered in vented crucibles for one hour in hydrogen at 2473 K [after Ref. 3].

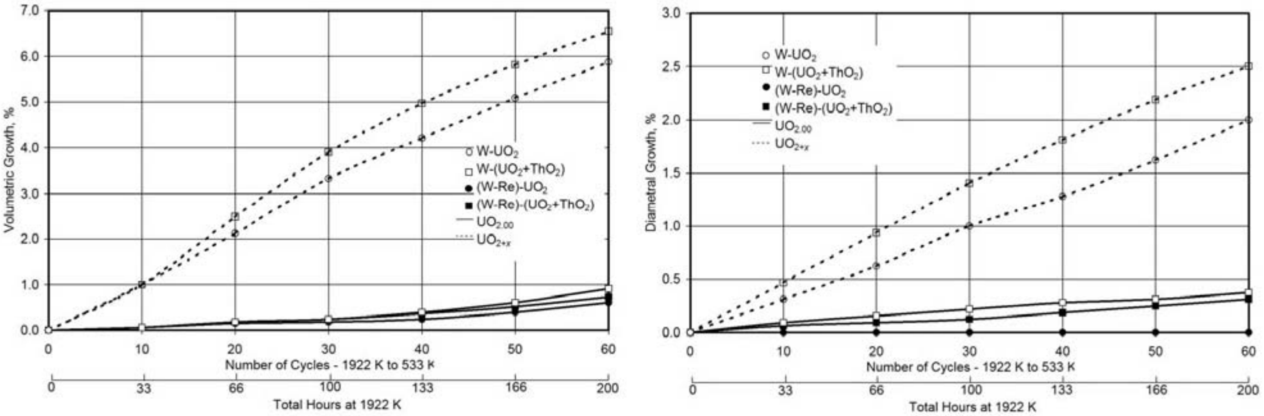

Fig. 2. Percentage of volumetric growth (left) and diametral growth (right) as a function of number of thermal cycles and total hours at 1922 K for different fuel stoichiometries [after Ref. 3].

Other issues, such as differences in the coefficient of thermal expansion between the fuel, matrix material and cladding, also presented themselves during this developmental program. During bonding of the cladding to the fuel, the cladding expanded two times more than the matrix containing the fuel, resulting in compression at the interface when cooled to room temperature. An element was often sectioned for metallographic analysis after thermal cycling and irradiation tests. Sectioning the sample relieved the residual stress present at the interface. These residual stresses present during testing produced highly localized stresses at the cladding-core interface adjacent to the section. Therefore, the interfacial zone between the cladding and matrix material was a potential area of weakness and could lead to element failure.

Thermal expansion differences were also exposed during thermal cycling, i.e. startup, normal steady-state and shutdown, in addition to any temperature cycle in between that was necessary for normal operation. Alloying with 3 wt% Re in the tungsten matrix increased the low-temperature ductility of the matrix and helped minimize or eliminate this potential, weak interfacial zone, shown graphically in Fig. 3.

Molybdenum was also investigated as a possible matrix material substitute for tungsten. However, preliminary investigations were not promising since the lower strength of Mo that caused increased swelling at high burnups from fission gas pressure buildup. Loss of Mo by volatilization at higher temperatures during the electron beam (EB) welding process for joining fuel elements and during thermal cycling was also undesirable, since this lead to phase shifts.

Overall, the major process establishments and improvements with GE 710 fuel fabrication were development of a continuous push-type sintering furnace rather than the batch furnace operation, identification of possible fuel stabilizers and determination of appropriate

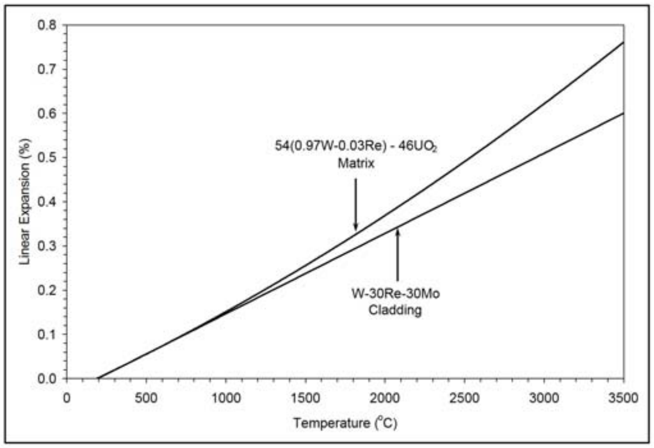

Fig. 3. Percentage of linear thermal expansion as a function of temperature for W-30Re-30Mo (nominal wt%) cladding and 54(0.97W-0.03Re) – 46UO_2 (nominal wt%) matrix material [after Ref. 3].

fuel stoichiometry, and development of the ideal matrix alloy to accommodate fission product buildup and thermal expansion differences.

II.B. Element Fabrication

Essentially, W-UO_2 CERMETs were cold pressed and sintered into segments of approximately 12.7 mm length followed by machining into a hexagonal shape. Coolant channels 0.914 mm in diameter were drilled into the hexagonal fuel element followed by placement of the fuel element in the selected 0.381 mm thick cladding material. Coolant tubes 0.203 mm thick were sealed into place at one end of the element by tungsten inert gas (TIG) welding and brazed directly into the header at the other end prior to complete element assembly. The outer hexagonal cladding was secured to the header plate by TIG welding. Fuel segments were protected from the braze material by a Ta spacer placed adjacent to the header plate. A high-pressure, high-temperature autoclaving process or hot-gas pressure process was employed to bond the CERMET fuel element to the cladding. Autoclaving was typically carried out at 10.3 MPa and 1922 K for one hour while the hot gas pressure bonding process typically involved exposure to 2022 K at 68.9 MPa for two to three hours. Shorter durations resulted in less bonding between the element and cladding but had reduced microstructural impacts on the cladding alloy, i.e. grain growth, re-precipitation, etc.

Multiple cladding materials were investigated during the GE 710 program, each with significant advantages and disadvantages. Of these, the most promising were elemental tantalum, tantalum alloys (T-111 and Ta-10 wt% W) and a W-30Re-30Mo (nominal wt%) alloy. Tantalum was selected as the initial cladding material mainly because the material was readily available in the required form and had sufficient compatibility for the intended application. Tantalum clad performance was limited by fuel stoichiometry since free uranium metal had a tendency to form reaction voids in the cladding. Reaction void formation was believed to be a solid-state diffusion phenomena because diffusion of Ta into W was much faster and diffused deeper than W into Ta. Hence, the fuel element lifetime was indirectly dependent upon fuel stoichiometry, of which UO_2 dissociation could be reduced but not eliminated, resulting in embrittlement of the protective cladding. Substoichiometric fuel remains single phase at a constant temperature, as described in the previous section. However, repeated temperature cycling from high to low temperature allows uranium metal to freely precipitate out of the single-phase UO_{2-x} and begin migration to and through the grain boundaries of the W matrix and eventually into the grain boundaries of the Ta cladding. Cladding thickness can be traversed with sufficient time, and leak paths can develop where the free uranium metal re-oxidizes to form the stable UO_2 compound. T-111 alloy (Ta-8W-2Hf nominal wt%) was considered as an alternative cladding material mainly because of previous use with Ta and Ta-10W within the GE High Temperature Materials Program and the GE 710 Program. T-111 maintains a fine grain structure (0.020 to 0.025 mm) after extended exposures to elevated temperatures, but is susceptible to grain growth at temperatures above 1922 K. Overall, the alloy maintains good creep resistance and high temperature strength, has a high ultimate strength and melting point, and has adequate ductility. However, disadvantages stem from the fact that the alloy has a high oxygen permeability that results in reaction void formations, and is extremely sensitive to gas impurity absorption, similar to disadvantages with the elemental Ta cladding. W-30Re-30Mo was considered an advantageous cladding material because of low oxygen permeability (low reaction void formation), low sensitivity to gas impurity absorption, high strength and melting point, and adequate ductility.[10] Oxygen diffusion through W-30Re-30Mo cladding was approximately three orders of magnitude lower than Ta, effectively increasing the service life for a given fuel element. However, high bond stresses that could have resulted in failure often occurred during thermal cycling due to the mismatch in thermal expansion between the fuel element and cladding alloy. Originally, a solution anneal heat treatment was carried out on the W-30Re-30Mo alloy. This heat treatment resulted in re-precipitation of the sigma phase in the alloy with increased time during testing. The phase re-precipitated preferentially at the grain boundaries and resulted in weakening of the cladding, limiting the strain capability. The cladding alloy was still subjected to a heat treatment during hot-gas pressure bonding, but this did not result in solutioning of the sigma phase and excessive grain growth. Furthermore, volatilization of Mo during high temperature exposures had a tendency to shift the W-30Re-30Mo alloy to a richer sigma phase composition and increase the phase formation, raising further concern for cladding strength. An absence of the sigma phase was found in the cladding-core diffusion zone that resulted from Re depletion by diffusion into and solutioning with the tungsten matrix.[11] Overall, the higher the content of free uranium in the fueled cores, the shorter the leak free life and the greater the number of cladding leaks, with significant amounts of free uranium defined as >1000 ppm.

Overall, the major process establishments and improvements with GE 710 element fabrication were development of numerical tap control drilling units, improvements in the diamond core-drilling operation for the fueled compacts, and more efficient and economical nuclear safe centrifugal filtration systems for the diamond core-drilling and surface grinding operations. More efficient fixturing and tooling decreased the impact of economics and increased the reproducibility involved with element fabrication. However, typical product yields were still low, ranging from 75 to 85%, with poor materials availability cited as the primary cause.

III. ANL NUCLEAR ROCKET PROGRAM

The Argonne National Laboratory (ANL) Nuclear Rocket Program sought to address three major issues: 1) identify the major advantages and limitations of refractory alloy fuels for NTP applications, 2) determine the performance to be expected of such fuels, and 3) further investigate the materials research and fuel testing associated with this fuel type. The reference design for the ANL Nuclear Rocket Program was two-fold: a 2000 MW topping cycle engine system providing up to 445 kN of thrust and a 44.5 kN thrust bleed-cycle system that would be applicable for low-thrust level missions. The designs consisted of a cylindrical core that was supported by Inconel Inco-718 grid plates at the cold end of the reactor. Beryllium oxide was situated in a cylindrical fashion to serve as an axial reflector at the inlet side of the core. A pre-heater consisting of stainless steel – UO_2 fuel elements was also used at the inlet side of the reactor core.

III.A. Fuel Fabrication

Three methods were investigated for fabrication of the fuel segments. The first was cold press and sintering of W-UO_2 wafers approximately 6.3 mm thick. Fuel wafers could be stacked on top of one another to compose a fuel column. By doing so, wafers could be stacked in such a manner as to grade the composition to optimize the physics and thermodynamics of the reactor core. This fabrication method demanded a high strength cladding material since a majority of the structural support would be imposed on the cladding and not the fuel column itself. The second method was powder-metallurgical preparation of long fuel elements by an isostatic sintering technique. This method offered the advantage of fabricating longer fuel elements at a single time, minimizing the concerns over tolerance associated with the coolant channels necessary for the wafer stacking method. Fuel elements fabricated in this manner were approximately 45.7 cm long per element. The final method investigated involved hot pneumatic compaction of vapor-deposited tungsten coated UO_2 particles. For all methods, a fuel loading of 60 vol%, UO_2 (93% ^{235}U) was used inside a W or W-Re matrix.

Similar to the GE 710 program, stabilizers were added to the UO_2 to inhibit dissociation and uranium migration to the cladding that ultimately resulted in cladding failure, and to reduce dimensional swelling during irradiation. However, stabilizers of interest for the ANL program included $GdO_{1.5}$, $DyO_{1.5}$, $YO_{1.5}$ and MoO_3. These stabilizers were found to be the most effective in the order that they were listed (high to low). Ten mole percent of the stabilizers were added to the UO_2 for all investigations conducted under this program. The powder metallurgical fabrication method was carried out by the Minnesota Mining and Manufacturing Company (3M), and although they were successful in providing reasonably dense CERMETs, dimensional tolerances were unacceptable for further consideration. CoorsTek (formerly Coors Porcelain Company) carried out the isostatic pressing method, and similar to 3M, were successful in fabricating shorter length fuel sections, but concerns over the feed material supply and dimensional controls were raised. Since most of the fabrication was carried out by third parties, and since information relating to the ANL program is still controlled, specifics relating to fabrication parameters are unavailable.

Induction brazing was investigated as a means to join fuel sections and/or wafers to fabricate a fuel element. ANL developed a number of metal alloy brazes with melt temperatures above 1973 K. Of these, a Zr-Mo alloy was the most successful. The induction apparatus was capable of working under both vacuum and an inert helium environment. However, gas generated by the matrix material during brazing made it virtually impossible to create a leak free joint. ANL devised a clever method to overcome this by immersing the fuel section in liquid nitrogen prior to brazing, with the section to be brazed left above the liquid pool. Brazing was carried out within five seconds to avoid allowing the fuel section coming to a temperature where volatilization of impurities could occur.

III.B. Element Fabrication

Two methods for cladding the CERMET fuel elements were devised under the ANL program. The first involved diffusion bonding W-25 wt% Re to the fuel element, using a technique similar to that used for the GE 710 program. Rhenium was desirable allowing tungsten to be more ductile and raising the brittle-to-ductile transition temperature. Although rhenium does not possess desirable nuclear properties for thermal reactor applications, fast reactor limitations are not prohibitive. In addition, the temperature of a W-25Re clad element must remain below 2222 K in order to avoid creep of the element. The hexagonal fuel section was placed in an extruded W-25Re can and thin walled W or W-25Re tubes were placed inside the coolant channels. The high temperature autoclave (diffusion bonding) was designed to operate at 2773 K and 34.3 MPa, but was never tested at this temperature and pressure. Rather, a temperature of 1923 K and a pressure of 10.3 MPa was used to diffusion bond the cladding. These parameters were found to be reasonably adequate for bonding.

The second method for applying cladding to the CERMET fuel elements was a vapor deposition process whereby a tungsten coating was applied to both the interior coolant channels and the exposed fuel element surface. Lengths of up to 0.145 m could be coated in the ANL apparatus and the coating was found to be of high purity and density. A 0.178 mm thick coating was applied to the coolant channels while a 0.381 mm thick coating was applied to the exposed surface at a deposition temperature of 773-823 K and a pressure of 400-440 torr. Concerns were raised about the columnar grain structure with the major axis being parallel to the growth direction for vapor deposited coatings. This structure was believed to present paths for free uranium migration and promote cladding attack, but preliminary tests on vapor deposited clad specimens did not reveal significant material losses. Another concern associated with vapor deposited coatings was the presence of fluoride in the cladding, but was found to be negligible.

IV. ALTERNATIVE FABRICATION METHODS

Although a number of NTP projects have been initiated since the 1960s, none have had any sustained fuel development work that appreciably contributed to fuel fabrication data. Under DOE's High Temperature Gas Reactor (HTGR) program and other fuels development programs, significant technology advancements have been made relative to the manufacture of microsphere fuel particles and protective coatings technology. Obviously, the first step necessary for recapture of CERMET fuel fabrication technology is establishment and enhancement of current fabrication methods capable of producing and reproducing quality fuel elements for rigorous testing. Dissociation of the UO_2 fuel particles has been shown to be the life limiting mechanism of the fuel element, since free uranium actively embrittles the cladding material. In addition, fission products, such as ruthenium and rhodium that tend to manifest themselves as metals, could diffuse out of the oxide fuel. Thermal cycling and grain growth resulting from high temperatures could result in fission product release sites along the grain boundaries. The DBTT can be increased in bcc metals (such as tungsten) through coarsening of the grain size. A lower DBTT, and thus finer grains, require decreased temperature ramp rates to minimize thermal stress.

Technology associated with UO_2 ceramic microsphere fabrication has been extensively developed over the past decade. As such, more advanced fuel fabrication processing techniques would address the fuel performance issues discussed above with specific ability to create highly uniform, spherical ceramic oxide particles with defined density and particle size (50-6000 μm range). Some examples of these methods include, but are not limited to, spray drying, press-sinter-crush, solution-gelation (sol-gel) and alginate precipitation. Powders with varying grain size distributions and odd shapes are undesirable because these properties can ultimately lead to agglomeration, inexact dosage, abrading with loss of material and low reproducibility of fabricated parts. Microspheres appear to be the most desirable type of particles because they are perfectly spherical, are of a monodisperse grain size, nonabrading and therefore dust free, free-flowing, porous with a large surface area and can be engineered to be either soft or hard.

A solution-gelation (sol-gel) process involving dropping uranyl nitrate (hydroxides and carbonates can also be used) solution into an appropriate hardening solution (pre-solidification with ammonia gas and solidification in ammonia solution) creating ceramic microspheres has been shown to be an effective fabrication method.[12] Basically, this process involves generating a laminar liquid flow through a vibrating nozzle to create droplets. The droplets originate and retain a spherical shape due to the high surface tension of the solution. The amount of initial solidification can be controlled by varying the reaction time and concentration of ammonia in the precipitation solution. Fabricated particles are washed to remove ammonia salts formed during gelation, dried in air, and calcined under hydrogen to improve particle density. Stabilizing compounds, such as thorium, gadolinium, hafnium, etc., could be included in the starting solution feedstock to prepare solid solution oxide microspheres. A flow chart outlining the pertinent steps of the solution-external gelation process is provided in Fig. 4. A second, similar fabrication process is the suspension process. Here, metal oxide powders with a fine grain size are suspended in water with a temporary binder. The suspension is molded employing a vibrational dropping process into an aqueous solution where the microspheres solidify. The microspheres are washed and dried followed by decomposition of the binder during a calcination step at 823 K. With this process, the use of corrosive ammonia gas and ammonia solutions can be eliminated. The most conventionally used binders are alginates.[14,15] These types of methods have been used to fabricate a number of ceramic and CERCER microsphere powders, examples of which can be found in Refs. 13 and 16-18.

Auto-Ignition Combustion Synthesis (AICS) is a process characterized by rapidly heating an aqueous solution containing metallic, organometallic (e.g. nitrates, phosphates, acetates) and/or organic (e.g. urea, stearic acid, carbohydrazide) components that trigger an exothermic reaction resulting in high purity micro- to nano-sized powders. The significant advantages of this fabrication method over traditional powder fabrication methods such as sol-gel synthesis and wet chemical synthesis include high temperatures achieved during reaction that volatilize any impurities and the organic components, and rapid heating and cooling times that minimize agglomeration experienced in the powder product(s), low cost and relatively safer starting components and simple, easy to use, commercially available fabrication equipment. For example, uranium oxide-cerium oxide ($[U_{0.72}Ce_{0.28}]O_2$) solid solutions have been fabricated from uranyl nitrate solution and cerium nitrate with citric acid employing AICS.[19] Powders fabricated with this technique were solid solution oxides of uranium and cerium after combustion was completed at 823K and had better sinterability characteristics than powders prepared employing a more complex and costly co-precipitation technique. Nanocrystalline, freely flowing, porous urania-thoria ($[U,Th]O_2$) solid solution powders have been similarly fabricated employing AICS from uranyl and thorium nitrates with citric acid organic fuel that are suitable as feed material for sintering high density fuel pellets,[20,21] as well as nanocrystalline ThO_2 powders with high sinterability characteristics using citric acid fuel[22] and glycine fuel.[23] Rare Earth (La, Nd and Sm) oxides that exhibit considerable solid solubility in UO_2 and aid in stabilization have been fabricated employing AICS from metal nitrates and urea.[24]

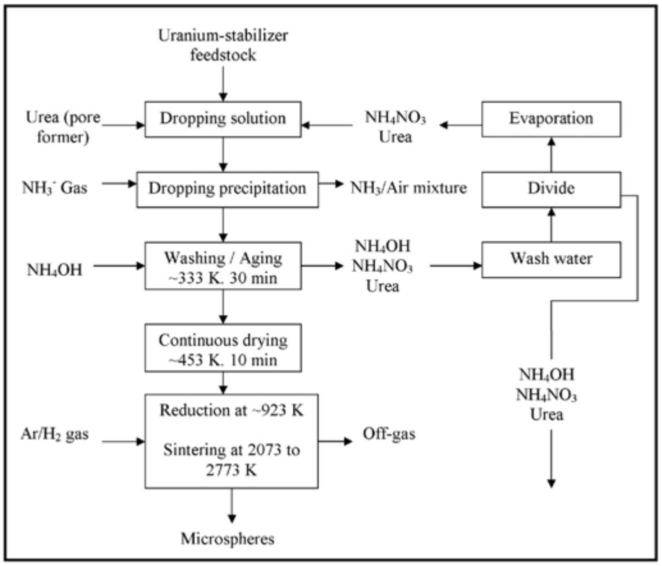

Fig. 4. Flow chart of the solution-external gelation process to fabricate UO_2 microsphere kernels [after Ref. 13]

Advanced processing techniques to incorporate the fuel particle into a metallic matrix in a manner capable of providing a specified product density with superior homogeneity and desirable material properties are advantageous over the more conventional and previously used processing methods, such as cold isostatic pressing (CIPing), sintering and hot isostatic pressing (HIPing). While these technologies are sufficient to recapture previous fabrication experience and provide an acceptable product, other, more advanced technologies exist that could improve the process quality of the fuel elements and address the quality control issues associated with fabrication. For example, Spark Plasma Sintering (SPS) is a technique to fabricate dense materials by pulsation of an AC or DC current through a reactant mixture while simultaneously applying a uniaxial pressure. As such, advantages over more conventional techniques such as hot-pressing and pressure-less sintering include lower sintering temperature, shorter hold time and marked comparative improvements in material properties that result in increased control of grain size, and therefore mechanical properties, and the ability to consolidate nanometric powders.[25] The SPS technique seeks to apply Joule heating to the reactant compact allowing high heating rates and minimizing surface diffusion mechanisms (e.g. Ostwald ripening) while applying the pressure that aids in particle re-arrangement and enhanced consolidation of the product.[26] In other words, kinetic mechanisms that typically dominate in the high temperature regimes necessary for fabrication of refractory CERMETs can be dramatically minimized with lower temperatures while producing a superior product to that of HIP or sintering employing SPS. More accurate control over the DBTT could be achieved in this manner, in addition to minimizing any initial dissociation of UO_2 that could occur at higher temperatures using conventional sintering or HIP. SPS has been demonstrated as a viable fabrication technique to consolidate both molybdenum and tungsten refractory metals.[27] Employing this technique, molybdenum was densified to between 96-98% theoretical and tungsten to between 90-92% theoretical at a temperature between 1573-1773 K, a pressure between 50-75 MPa and a hold time at temperature no greater than three minutes. Grain growth during fabrication was negligible, slightly increasing for higher temperatures and applied pressures. Any porosity present after consolidation tended to manifest itself at the center of the compact. This could be advantageous for CERMETs with pores accommodating fission product generation while maintaining the structural integrity at the radial edge of the product. Addition of small amounts of Re, such as that done for previous campaigns, could increase the sintered density further, if necessary. One disadvantage of SPS is the maximum sample dimensions that can be fabricated at a single time. Employment of this process would most likely require fuel wafers to be stacked and bonded to create the fuel element, similar to aspects of both the GE 710 and ANL programs. A similar technique of Joule heating, although employing non-pulsating DC current and therefore distinguishing itself from SPS, was investigated to fabricate W-ZrO_2 [surrogate for UO_2] CERMETs.[28] Fabricated samples displayed a high degree of sintered tungsten particles within five minutes of exposure to the current under applied load. Two significant issues associated with this process were identified. Dispersed throughout the pellet matrix was a second phase, possibly WO_x, due to air being trapped within the sample. The second issue was the dissociation and plastic deformation of ZrO_2 which was observed in all samples because maximum temperatures were greater than 2473 K. These two issues are process controllable conditions and can be resolved by introducing a stabilizing compound to the fuel particle and employing a pulsed current rather than a continuous current.

Technology development for other welding and joining techniques is also important. High temperature refractory brazing alloys were developed under the ANL program, but application with newer, less conventional fuel element fabrication techniques might require additional refinement. Additional brazing compounds, such as Pt-10Rh, have been proposed as a possibility for joining sections of fuel wafers. Solid-state diffusion bonding of W-25Re alloys using nickel as the interleaf material forming a Ni-W-Re ternary has been demonstrated at temperatures as low as 1173 K, although a temperature of 1773 K is required to produce a sufficiently strong bond.[29] Brazing of refractory metals is generally undesirable owing to recrystallization of the microstructure produced in the joint. Solid-state diffusion bonding (SSDB) overcomes this limitation by accomplishing bonding at a significantly lower temperature thereby avoiding recrystallization. Although nickel might be an undesirable interleaf material for the higher temperature NTP applications, similar SSDB interleaf materials may exist and should be investigated.

IV. CONCLUSIONS

The current paper seeks to address CERMET fuel fabrication for NTP applications. Brief descriptions of the two major CERMET fuel fabrication campaigns, the GE 710 program and the ANL Nuclear Rocket program, have been provided. In addition, suggestions for less conventional, more advanced fabrication processes both for UO_2 ceramic fuel and the metallic matrix have been discussed. Admittedly, these technologies are on the cusp and require more research than the recapture technologies that demand only further development. However, the amount of research required to advance these technologies to the point of becoming effective NTP fuel fabrication methods can be perceived as small and well-worth the investment, particularly if they produce a far superior product capable of meeting the high expectations of mechanical and structural integrity, and fission product retention. Fabrication and evaluation of new fuels fabricated with new processes requires that researchers know and understand key characteristics, such as thermo-physical and chemical properties, mechanical properties particularly at elevated temperatures, and microstructural features. In addition, such processes demand that researchers understand previous development efforts, and that future researchers are capable of relating to and understanding both former and current investigators in the area of space fuels research. Future interest in nuclear propulsion is dependent upon a combination of a good sense of history, and an intuition to continually develop and build upon the established fuel fabrication foundation.

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