Combustível composto avançado UO₂-UN com condutividade térmica melhorada e alta densidade

(Advanced composite fuel UO₂–UN with enhanced thermal conductivity and high density)

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Abstract

Today, many efforts focus on ceramic fuels that can replace standard uranium dioxide (UO_2). In this context, uranium nitride (UN) could replace UO_2 used in light water reactors (LWRs). The UN fuel has a higher uranium density and better thermal conductivity than UO_2. The drawback of UN is a lower oxidation resistance in contact with the water. Regardless, adding a compound that acts as a protective barrier against nitride oxidation, such as ZrN, U_3Si_2, and UO_2, could reduce water oxidation. Early, UO_2–UN composites were fabricated by hot pressing UO_2–UN powder mixtures within 1300 °C–1590 °C. The manufacturing process adopted for the fuel pellet fabrication changed to the spark plasma sintering (SPS) method. Using SPS can avoid the exceptional resistance to producing a perfect microstructure and the high costs associated with 15N enrichment. The composite fuel suggested is UN-10% U_3Si_5 verified with FRAPCON code.

Keywords: Uranium Mononitride, Uranium dioxide, Spark Plasma Sintering

INTRODUCTION

Worldwide interest is growing in actinide nitrides as fuel schemes for various reactor types. Uranium nitride, UN, not be the principal candidate but is a new monolithic fuel choice for LWR because it contains a very high uranium density, which is excellent for updating existing plants [1]. Therefore, the UN could fail under accident conditions when exposed to water. In the open literature, growth reports have used UN fuel as the primary phase, with tiny fractions of U_3Si_5, U_3Si_2, UB_4, or ZrO_2 as the secondary phase [2]. The benefits were partly because of their increased U-density and above-average thermal conductivity over standard UO_2. The composite fuels studied are UN-U_3Si_5, UN-U_3Si_2, UN-UB_4, and UN-ZrO_2 to replace UO_2 in Pressurized Water Reactor (PWRs), Boiling Water Reactors (BWRs) and suggested for supercritical water reactors.

Pure nitride fuels are undesirable in PWRs because of rapid chemical reactions with water but additions of a secondary phase using silicides. The U_3Si_5 phase in the UN–U_3Si_5 fuel concept shields the nitride phase from water. The synthesis route used for UN and U_3Si_2 composites is the conventional vacuum sintering, but the silicide phase shows significant micro-cracks due to a difference in their thermal expansion. Both U_3Si_2 and U_3Si_5 offer similar chemical bonds [3]. In contrast, the U_3Si_5 shows a phase change at 450 °C, is a brittle metal, provides a high melting point of 1770 °C, and is strongly anisotropic.

Over the years, many experiments have used additive phases mixed with UN, creating a shield layer against water effects. These additives produce UN-Zr, UN-Y, UN-Ti, and UN-Cr that will react with UN by removing nitrogen and resulting in metallic uranium. Besides, a second phase may also show desirable oxidation resistance, physical properties, neutron absorption, and the ability to react with the UN matrix chemically. The use SPS route allows for lower sintering temperatures with high density, which is an advantage compared with the conventional sintering techniques [4]. In contrast, the metallurgic route applied to U_3Si_2 uses uranium and silicon through arc melting, employing silicide grain coating and nitride waterproofing, with a density reaching 98%TD fabricated using (SPS) method at 1450°C . The advantages generated by SPS for UN-U_3Si_2 (10%) composites show a density range (96–99)% TD and grain size range (6–24) μm, which could avoid the micro-cracks significantly.

UN has a crystal structure like NaCl-type or Face-Centered Cubic (FCC) structure with a lattice parameter length of 0.4889 nm. Uranium nitride, compared with UO_2, has superior features comprising a theoretical density of 14.30 g/cm^3, thermal conductivity of 13 W/m-k, and a melting point of 2365 °C. The high density of the uranium allows for long burn cycles and reduced enrichment. Undesirable facts exist, such as oxygen and water vapor can react with the UN and speed up the decomposition at over 1300 °C. Natural nitrogen has two stable isotopes, N-14, with an abundance of 96. 636% and N-15 of 0.364%. However, it had used the isotope N-15, which is more desirable because the isotope, N-14, shows a particular absorption cross-section ($\sigma_a^{N14} = 10^5 \sigma_a^{N15}$). It undergoes an (n, p) reaction, which produces the isotope C-14 radioactive. UN in LWRs permits reviewing a more robust cladding material as iron-chromium-aluminum (FeCrAl) alloy by providing more uranium loading, equalizing for possible increased neutron absorption [6].

<u>Fuel performance code</u>

The fuel codes have the mission of helping to license new nuclear units. A few tools, such as FRAPCON, BISON, TRANSURANUS, and FALCON, can predict the fuel response of the steady-state thermal-mechanical behavior. The Nuclear Regulatory Commission (NRC) and the Pacific Northwest Laboratory (PNNL) recommend the FRAPCON code for the licensing process [7]. Today, FAST is the current NRC thermal-mechanical fuel performance code, an evolution of FRAPCON, containing transient capabilities from FRAPTRAN. The library of material properties includes fuel density, thermal conductivity, specific heat, enthalpy, and mechanical response as elastic modulus. It calculates the fuel rod features over time, including fuel and cladding temperature, cladding hoop strain, cladding oxidation, fuel irradiation swelling, fuel densification, fission gas release, and fuel rod internal pressure.

MATERIAL AND METHODS

The thermal properties of the mixed fuels are the central points of the fuel codes. In this study case, it must determine the physical properties of composite fuels uranium silicide-nitride applying mixture rules. The Kopp–Neumann rule (KNR) has been extensively used to calculate the heat capacity of ceramic composites. Vegârd's law is valid in multiphase solid

solutions with similar crystallography. Fuels composed of UN and U_3Si_2 or U_3Si_5 will substantially increase the thermal conductivity of the fuel over pure UO_2. Various compositions vary from (50 wt.% to 90 wt.%) UN and (10 wt.% to 50 wt.%) U_3Si_2 display improvements depending on the formulation. However, composite fuels' physical properties are fundamental points to fuel performance codes. Equation (A) represents Vegard's law for a solid solution, for example, UN_x-$U_3Si_{2(1-x)}$.

$$A_{(UN_x - U_3 Si_{2(1-x)})} = A_{(UN)} \times x + A_{(U_3 Si_2)} \times (1-x) \qquad \text{(A)}$$

where A is the lattice parameter, x is the fraction of UN in the first phase, and (1-x) represents the second phase U_3Si_2.

Physical properties of uranium and nitride silicide

The heat transfer equations have three related properties, which are thermal conductivity (k), thermal diffusivity (α), and specific heat capacity (Cp), valid for pure and composite materials with composites, must use the empirical KNR. Equation (B) generically describes the relationship between the described properties.

$$k = \alpha \times \rho \times C_p \qquad \text{(A)}$$

where α is the thermal diffusivity (m²/s), k represents thermal conductivity (W/m-K), C_p is the specific heat (J/kg-K), and ρ expresses the density (kg/m³), and.

Thermal diffusivity describes the speed at which heat travels through a material. Table (I) shows the physical properties of uranium nitride, uranium dioxide, and uranium silicide at 25 °C.

Table I: Physical properties of uranium-based ceramic fuels.

Uranium compound	UN	U_3Si_2	UO_2
Density (g/cm³)	14.30	12.20	10.96
Uranium content (gU/cm³)	13.50	11.30	9.60
Melting point (°C)	2850	1665	2865
Thermal conductivity (W/m k)	14.0	8.0	7.50

U_3Si_2 ceramic oxide provides a higher uranium load than UO_2, which allows longer irradiation cycles to be endured. Silicides have a uranium density of around 17% higher than that of UO_2. The physical properties of UN are like those of U_3Si_2, showing high thermal conductivities that increase with temperature [8]. In the following empirical correlations, equation (C) calculates the thermal conductivities of UN fuel as a function of the temperature. Equations (D) and (E) represent the thermal conductivity of the composite fuel U_3Si_2.

$$k_{UN}(T) = (-17.75 + 0.08808T - 6.161 \times 10^{-5}\,T^2 + 1.447 \times 10^{-8}T^3) \times \frac{1-p}{1+p} \quad \text{(C)}$$

where p is porosity valid $0 \leq p \leq 0.1$, $k(T)$ is the thermal conductivity as a function of temperature, and T represents the temperature in K valid into range ($680K \leq T \leq 1600$).

$$K_{U3Si2}(T) = 7.98 + 0.0051 \times (T - 273.15) \qquad (T \leq 1473.15\ K) \qquad \text{(D)}$$

$$K_{U3Si2}(T) = (6.1 \times 10^{-3} \times T + 9) \times \left(\frac{1-p}{1+2.5p}\right) \qquad (T \geq 1773\ K) \qquad \text{(E)}$$

where $k(T)$ is the conductivity in W/m-K, p is the porosity, and T is the temperature in K.

Thermal stress generates diametral cracks in the pellet, resulting in fuel spraying during long burn cycles. The Bison code adopts the following correlation for linear thermal expansion as polynomial fitting described in equation (F) also equations (G). Then, equation (H) is an empirical correlation for U_3Si_2 that expresses the coefficient of thermal expansion as a function of temperature in K.

$$\alpha_{UN}(T) = 3.8 \times 10^{-11}\,T^3 - 7.6 \times 10^{-8}T^2 + 5.8 \times 10^{-5}T - 1.2 \times 10^{-2} \quad \text{(F)}$$

$$\propto_{UN}(T) = 7.096 \times 10^{-6} + 14.093 \times 10^{-10}T \qquad (298\ K \leq T \leq 2523K) \qquad \text{(G)}$$

$$\alpha_{U3Si2}(T) = 15.7 - 0.002 \times (T - 273.15) \times 10^{-6} \quad (298K \leq T \leq 1900K) \qquad \text{(H)}$$

The specific heat of UN used for the fuel performance codes agrees with the equation given from the Matzke model. However, advanced fuels exhibit reduced thermal capacity compared to UO_2. The specific heat capacity of UO_2 at room temperature is 235 J/kg k higher

than that of U$_3$Si$_2$, equal to 202 J/kg K, and for UN it reaches 190 J/Kg-k [9]. Equation (I) expresses the heat capacity in (J/kg K) as a function of the temperature in K, and equation (J) represents the exact correlation for uranium silicide.

$$Cp_{UN}(T) = (\frac{1}{0.252})(54.1 + 2.28 \times 10^{-3}T + 4.37 \times 10^{-6}T^2 - 6.81 \times 10^5 T^{-2} \quad \text{(I)}$$

$$Cp_{U3Si2}(T) = 190 + 0.104(T - 273.15) \quad \text{(J)}$$

where C_p is the heat capacity in (J/kg-K), T is the temperature in K in the range (298 K – 2573 K).

Fuel enthalpy is a metric applied to analyze the design basis for an accident-initiated reactivity. Equation (K) is the fuel enthalpy obtained by integrating the heat capacity of 298 K at the analyzed temperature. Equation (L) is an empirical correlation defined as the heat capacity integral expressing fuel enthalpy (J/kg) as temperature functions in K.

$$H(T) - H(298\ K) = \int_{298}^{T} C_p(T)dT \text{ (K)}$$

$$\Delta H(T) = \frac{51.14}{\exp(\frac{\theta}{T})-1} + 4.746 \times 10^{-3}T^2 - 8148.34 + 1.461 \times 10^7 \exp\left(\frac{-18081}{T}\right) \quad \text{(L)}$$

where $\Delta H(T)$ is fuel enthalpy in J/mol-K, θ is the Einstein temperature of uranium nitride, 365.7 K, with the valid in the range (298 K to 2628 K).

The thermal and mechanical properties of uranium nitride prepared using the SPS technique are better than those of the standard synthesis method. The elastic modulus of UN reaches 175 GPa, and the Poisson ratio is 0.34 at room temperature. Equation (M) is the young's modulus given as a function of temperature and density, valid, and D is density in TD, 70% $\leq$ D $\leq$ 100%. Equation (N) is the poison ratio in the function of density in TD.

$$E = 2.58 \times 10^5 D^{3.002}(1 - 2.375 \times 10^{-3}T) \quad (293\ K \ \leq T \leq 1473\ K) \text{ (M)}$$

$$v = 1.26 \times 10^{-3}D^{1.174} \quad \text{(N)}$$

where E is the elastic modulus in GPa and v is the Poisson ratio, which is dimensionless.

The irradiation properties of monolithic UN are more researched than those of uranium silicides. They have limited fission gas release (FGR), irradiation swelling, and irradiation creep models available in the literature [10]. Currently, the irradiation helps to swell, and it coded creep models in FRAPCON. Equation (O) describes the volumetric swelling correlation for UN fuel in the operational temperature range.

$$\frac{\Delta V}{V_0} = 4.7 \times 10^{-11} T_{avg}^{3.12} Bu^{0.83} \rho^{0.5} \quad (1200K \leq T \leq 1600K) \quad (O)$$

where T_{avg} represents the average temperature of the fuel in K, Bu is the fuel burnup at %, and ρ is the as-fabricated fuel density around 95% TD.

In fast reactors found, an advantage of nitride fuels is a lower gas release rate than for oxide and metal alloy fuels. Equation (P) suggested from several measures of fission gas release (FGR) from UN nuclear fuel given as a function of average fuel temperature.

$$R = 100/(\exp\left[0.0025\left(\frac{90D^{0.77}}{Bu^{0.99}} - T\right)\right] + 1) \quad (P)$$

where R is the FP gas release rate in percentage, the fuel pellet density in (% TD), Bu the burnup in fission per initial metal percent (FIMA%), and the temperature given in K.

<u>Influence of manufacturing process</u>

Uranium Nitride has exceptional resistance to sintering and subsequent difficulty in producing a desirable microstructure. The space power reactor program used a carbothermic-reduction/nitriding process to synthesize UN powders using conventional cold-pressing and sintering [11]. The manufacturing process employs the spark plasma method. Using SPS can avoid the excellent resistance to producing a superb microstructure and the high costs associated with N-15 enrichment. Various studies have found that SPS makes a material with good porosity and a perfect grain size. Composite pellet fuel using UO_2-33vol% UN established a density increase of 13% and enhanced thermal conductivity of up to 100% at 800 °C. The SPS permits easy densification of nitrides with no deterioration of thermal properties and is desirable as a preparation method for nitride fuels compared with conventional sintering methods.

RESULTS AND DISCUSSION

Inserting new physical properties following Vegard's law can execute the planned simulation, creating a new version of FRAPCON. The fuel used was conventional UO_2, pellet outside diameter 9.132 mm, pellet length 11 mm with an enrichment of 3.5%, using zircaloy as cladding. In contrast, it holds another mechanical dimension of the fuel and cladding. Still, the enrichment slightly reduces the regulation of the excess reached by the neutron multiplication factor. Thus, composite fuel was changed to (UN-10% U_3Si_5) fuel, where the manufacturing route adopted the SPS method, and ferritic Kanthal APMT substituted zircaloy-4. Figure (1) shows the average fuel temperatures of UO_2, $UN-U_3Si_2$, and U_3Si_2.
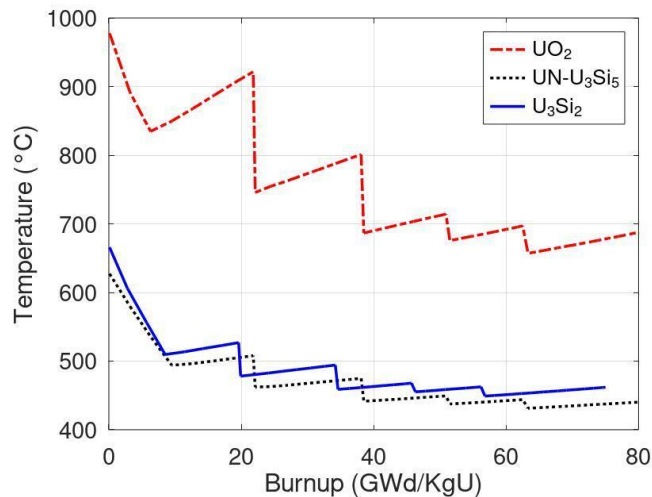

Figure 1: Average fuel temperatures of UO_2, $UN-U_3Si_5$, and U_3Si_2.

Following recommendations for more tolerant fuels, Un-U3Si5 can operate more efficiently because of lower fuel temperatures. The thermal and mechanic behavior of UN–U3Si5 fuels using Kanthal APMT as cladding show similar reactor physics and fuel management performance over a vast parameter space of phase fractions compared to UO2–Zr fuel–cladding. Measurements of U_3Si_2 have suggested that it possesses a thermal conductivity vastly superior to that of UO_2 when prepared by arc melting. The thermal conductivity of pure UN is about 4 to 8 times greater than that of UO_2 in the temperature range of the steady-state operation of PWRs. The thermal expansion of U_3Si_2 has a temperature dependence and is like U_3Si_5. Also, show a higher thermal expansion coefficient. Figure (2) shows the time response for gap closure.
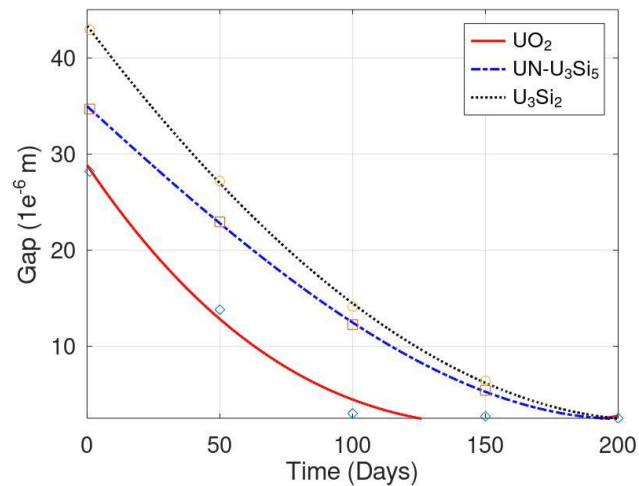
Figure 2: Structural radial gap, space between fuel pellet and cladding

The dimensional expansion contributes to swelling and pellet cladding interaction (PCI), which is critical to safe operation. Cladding fracture caused by PCI in PWR is an effective speed up for gap closure. After PCI, the mechanical behavior changed because of the stress growth, making the solid contact speed up the stress corrosion cracking. Figure (3) displays fuel stack elongation during the burn cycle.
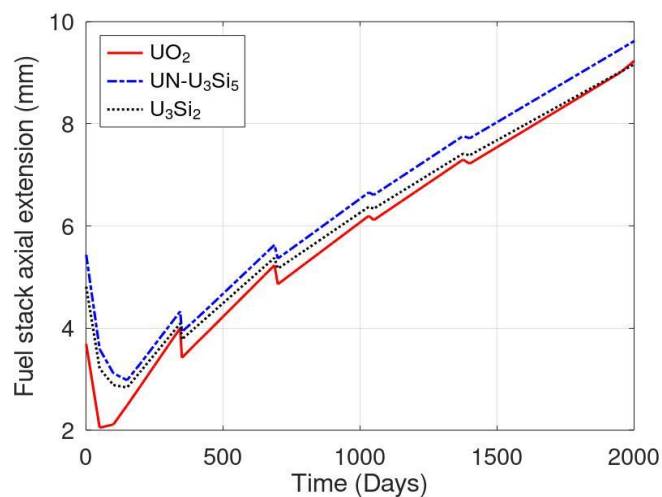

Figure 3: Fuel stack response given as temperature functions .

Under steady state, the mechanical strength of FeCrAl alloys is superior to the zircaloy. While zircaloy has ultimate tensile strength (UTS) of 413 MPa and yield tensile strength (YS) of 241 MPA, Kanthal APMT reaches UTS of 740 MPa and YS of 540 MPa. Besides, the elongation break limit of ferritic alloys is excellent compared to zircaloys.

CONCLUSION

Recently, several studies have proposed uranium silicide-nitride (UN–U_3Si_2, UN–U_3Si_5) composites fuels because of their increased uranium density with higher thermal conductivity and the ability to avoid UN degradation in contact with water. Possibly, the Kanthal[®] APMT with composition, (Fe (10–13)%, Cr (3–5)%. Al (0.03–0.07)%, Y (16–19) ppm) will be the change for zirconium alloys as cladding. Under accident scenarios, nitride fuels will produce lesser stored energy in the fuel. The ferritic alloys are safer under a loss of coolant accident, leading to severe material damage because of the rapid steam oxidation.

ACKNOWLEDGMENT

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