URANIUM NITRIDE AND SILICIDE COMPOSITE FUELS USED TO REDUCE FUEL OXIDATION

Daniel de Souza Gomes
Instituto de Pesquisas Energéticas e Nucleares (IPEN)
São Paulo, SP, Brasil
Abstract: In the 1960s, the space nuclear program for developing reactor propulsion designs led to uranium mononitride (UN) exploration as a fuel. Since then, the UN has gained traction because of its superior thermal conductivity and uranium density compared to standard UO$_2$. Reactors using sodium and lead as liquid coolants have a long history with UN fuel. More recently, a combination of uranium UN and uranium silicide (U$_3$Si$_2$) has emerged as a promising fuel option for power units. This composite fuel offers enhanced tolerance and resilience. However, several silicide compounds exist, such as USi, USi$_2$, USi$_3$, U$_3$Si, U$_3$Si$_2$, and U$_3$Si$_5$. Instead, they use nitride-silicide composites, such as UN-U$_3$Si$_5$. The UN-U$_3$Si$_5$ fuel, which features a secondary fissile phase with an elevated uranium density, has garnered significant interest. In this study, we compare the performance of UN-U$_3$Si$_2$ and UN-U$_3$Si$_5$ using Kanthal APMT as cladding.

Keywords: Uranium nitride, uranium silicide, accident tolerant fuel FRAPCON

INTRODUCTION

For the past four decades, uranium dioxide (UO$_2$) has been the standard fuel in light water reactors (LWRs). However, because of their high thermal conductivity and specific heat, uranium silicides have shown promise as potential substitutes for UO$_2$. Fuel options that use the U-Si system based on seven intermetallic compounds (USi, USi$_2$, USi$_3$, U$_3$Si, U$_3$Si$_2$, U$_3$Si$_4$, and U$_3$Si$_5$) have numerous benefits [1].

Investigations into ferritic alloys as potential replacements for zirconium alloys have revealed poorer neutronic performance. Furthermore, it has prompted attempts to thin the cladding and increase the amount of $^{235}$U enrichment. Composite uranium nitride with uranium silicide is an innovative, more tolerant fuel. Since the space reactor program invented high-temperature and fast-breeder designs in the 1960s, uranium mononitride (UN) fuel has become highly sought-after. Nitride has gained popularity because of its greater melting temperature than UO$_2$, fissionable density, strong thermal conductivity, and superior melting temperature over UO$_2$. Fast reactors cooled by lead and sodium, and those using liquid metal coolants frequently use UN fuel.

For the past decade, the accident-tolerant fuel (ATF) plan has been at the forefront of fuel development, exploring uranium silicide mixed with uranium nitride [2]. This plan has focused on finding advanced properties, such as higher uranium density and a thermal conductivity of 52 W/mK. The UN-U$_3$Si$_2$-UB$_2$ composite fuel was a vital component of an earlier, less harmful fuel plan [3]. At 300 °C, the additive UB$_2$ has a much higher thermal conductivity of 25 W/K than UO$_2$, 7 W/mK. It also has good corrosion resistance.

Notably, U$_3$Si and U$_3$Si$_2$ have higher uranium densities. Compounds like U$_3$Si$_5$ will be substituted for U$_3$Si$_5$ because irradiation resistance. These compounds have a minor effect on the energy interaction with steam and keep the nitride phase safe from water reactions. Compared to U$_3$Si$_2$ and U$_3$Si, U$_3$Si$_5$ has a higher silicon content (62.5%) and a lower uranium density. To compare UN-U$_3$Si$_2$ and UN-U$_3$Si$_5$, we use ferritic alloys, iron-chrome-aluminum (FeCrAl), as cladding [4]. Isotope $^{10}$B presents a thermal neutron cross-section of 3800 barns. Today, the UN uses uranium diboride (UB$_2$) as a second phase for ZrB$_2$ to suppress initial fuel reactivity [5].

In the last decades, the ATF's plan has tried many different ceramic mixes, including uranium dioxide-diboride (UO$_2$-UB$_2$), uranium nitride (UN), uranium silicide (U$_3$Si$_2$), and UN-U$_3$Si$_2$-UB$_2$. ATF has tried to find advanced properties, including a higher uranium density and a thermal conductivity of 52 W/mK. Composite uranium nitride...
with uranium silicide is an innovative, more tolerant fuel.

UN fuel has been in high demand since the space reactor program began with high-temperature and fast-breeder designs in the 1960s. Nitride has gained popularity because of its greater melting temperature than UO$_2$, fissionable density, strong thermal conductivity, and superior melting temperature over UO$_2$. Fast reactors cooled by lead and sodium, and those using liquid metal coolants frequently use UN fuel.

**MATERIAL AND METHODS**

Our investigation aims to enhance the FRAPCON code's physical characteristics to perform advanced simulations based on the material properties library [6]. This research is critical for developing more efficient and safer nuclear fuel systems, and zircaloy cladding is an essential element for standard fuel systems.

For the temperature range where PWRs are steady, UN-U$_3$Si$_2$ and UN-U$_3$Si$_5$ are about 5 to 7.5 times better at conducting heat than UO$_2$. Comparative gap closure occurs in about 200 days for UN-U$_3$Si$_2$ and UN-U$_3$Si$_5$ and about 100 days for UO$_2$ [7]. For safe operation, the pellet-cladding interaction (PCI) is critical. PCI causes cladding fracturing because the high temperatures accelerate the gap closure in PWR. The dimensional expansion facilitates swelling and PCI.

**FUEL SYSTEM PROPERTIES**

We used standard UO$_2$ fuel in this study, which had an enrichment of 3.5%, a pellet length of 11 mm, and an outside diameter of 9.132 mm. Table 1 depicts the physical properties of popular materials used in nuclear fuel systems [8–10].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Melting point (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>Thermal conductivity (W/m-K)</th>
<th>Heat capacity (J/kg-K)</th>
<th>Thermal expansion (µm/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
<td>2850±30</td>
<td>10.96±0.1</td>
<td>8.68±0.5</td>
<td>235±5</td>
<td>9.76±0.5</td>
</tr>
<tr>
<td>U$_3$Si$_2$</td>
<td>1665±20</td>
<td>12.2±0.1</td>
<td>16.3±0.5</td>
<td>202±5</td>
<td>15.2±0.5</td>
</tr>
<tr>
<td>U$_3$Si$_5$</td>
<td>1770±10</td>
<td>8.97±0.1</td>
<td>9.32±0.5</td>
<td>195±5</td>
<td>10.6±0.5</td>
</tr>
<tr>
<td>UN</td>
<td>2850±30</td>
<td>13.61±0.1</td>
<td>15.0±0.5</td>
<td>239±5</td>
<td>12.5±0.5</td>
</tr>
<tr>
<td>Zircaloy</td>
<td>1850±10</td>
<td>6.56±0.1</td>
<td>21.5±0.5</td>
<td>285±5</td>
<td>6.0±0.5</td>
</tr>
<tr>
<td>APMT</td>
<td>1450±10</td>
<td>7.25±0.1</td>
<td>11.0±0.5</td>
<td>480±5</td>
<td>12.4±0.5</td>
</tr>
<tr>
<td>SS-348</td>
<td>1450±20</td>
<td>8.00±0.1</td>
<td>16.3±0.5</td>
<td>500±5</td>
<td>17.7±0.5</td>
</tr>
</tbody>
</table>

Table 1: Physical properties of advanced fuel materials

Our intended composite fuel was (UN-80%-U$_3$Si$_5$-10%), and we used a ferritic alloy (Kanthal APMT). This type of FeCrAlMo alloy is a dispersion-strengthened ferritic iron-chromium-aluminum alloy. It is made up of Fe, Cr (21%), Al (5%), and Mo (3%).

The Spark Plasma Sintering (SPS) type can operate at lower temperatures for shorter processing times. By taking a quicker sintering path, UN-U$_3$Si$_5$ can be produced without going through the ternary phase [11]. Compared to U$_3$Si$_2$, the U$_3$Si$_5$ phase resists oxidation and behaves like UO$_2$. On the other hand, radiation causes crystal amorphization in U$_3$Si$_2$ and U$_3$Si.

This study used Kanthal APMT as the cladding material because of its superior resistance to oxidation and corrosion, two critical issues when using uranium nitride and silicide composite fuels. The second phase also presents another mechanical aspect of the fuel and cladding. The MatLib includes subroutines for fuel density, thermal conductivity, specific heat, enthalpy, mechanical reaction, and creep rate.

The ATF plan has evaluated composites with monolithic UB$_2$, such as UO$_2$-UB$_2$, U$_3$Si$_2$-UB$_2$, and UN-U$_3$Si$_5$-UB$_2$. UB$_2$ has advanced features, such as 30 W/mK thermal conductivity and a higher uranium density. The thermal neutron cross-section of isotope $^{10}$B is 3800 barns. Figure 1 depicts several
ATF materials’ thermal conductivities as temperature functions.

\[ \text{Specific heat capacity (J/kg·°C)} \]

\[ \text{Thermal conductivity (W/m·K)} \]

Figure 1. (a) Thermal conductivity of ATF fuel and (b) specific heat capacity.

However, we used an empirical isotopic ratio of \(^{10}\text{B}/^{11}\text{B}\) with UB\(_2\) enriched with \(^{11}\text{B}\), which has a substantially lower cross-section (0.0055 b).

In recent decades, researchers have used the arc-melting process, combining UN and U\(_3\)Si\(_2\) powders. However, U-Si-N systems have shown a few unknown ternary phases produced at high temperatures, which is a significant challenge. Understanding the properties and behavior of these unknown phases is crucial, as they can impact the fuel’s performance and safety. U\(_3\)Si\(_5\) is a magnetic and brittle metal whose electronic contribution dominates thermal conductivity at high temperatures.

Compared to U\(_3\)Si\(_2\) (11.3 gU/cm\(^3\)), U\(_3\)Si\(_5\) has a lower uranium density (7.5 gU/cm\(^3\)) but a better melting point and thermal conductivity than UO\(_2\). The composite UN-U\(_3\)Si\(_5\)’s neutron performance is comparable to that of UO\(_2\). A higher fissile density allows for an extended burning cycle, which is beneficial. The Fukushima Daiichi nuclear accident, with its rapid Zr-steam reaction in a high-temperature environment that fully exposed Zr alloys, generating large amounts of hydrogen and causing exothermic heating and blasting, underscores the importance of our research. The fuel used was the standard UO\(_2\), with an enrichment of 3.5%, a pellet length of 11 mm, and an outside diameter of 9.132 mm.

ACCIDENT MORE TOLERANT MATERIALS

Zircalloys, made of zirconium, have a low thermal neutron absorption cross-section, good corrosion resistance, and excellent dimensional stability in an irradiation environment. However, they have several drawbacks, such as cladding embrittlement and undesirable exothermal oxidation above 1204 °C.

Zircaloy replacement shows two options: Next-term, ferritic alloys mixed composed of iron-chromium (20–30%) and aluminum (4–7%), known as FeCrAl alloys; next-term Kanthal APMT, and long-term use of silicon carbide (SiC) fiber-reinforced. Figure 2 shows the creep rate of ATF materials’ elastic modulus and uranium silicide.
Consequently, it can release an enormous amount of hydrogen, followed by an explosion. Thus, ATF plans have investigated how to shield the cladding materials by adding Cr, Al, and Si elements from deep corrosion above 600 °C in the air using Cr$_2$O$_3$, Al$_2$O$_3$, or SiO$_2$ layers, which offer the best corrosion resistance.

ATF envisions implementing SiC fiber-reinforced SiC matrix (SiC/SiC) composites with two or three layers to replace zircaloys in the long term. SiC cladding reacts with water and steam 10,000 times more slowly than zirconium alloys, avoiding hydrogen and accidents.

On the other hand, austenitic stainless steels (SS), such as SS-316, have superior thermal conductivity and mechanical strength compared with zirconium-based alloys. Despite their low melting point of approximately 1450 °C, they outperform zircaloys with a melting point of roughly 1850 °C and UO$_2$ with a melting point of 2800 °C. The ferritic alloys show good features, such as thermal conductivity, which is somewhat better than zircaloys' in the temperature range of 373 °C to 1165 °C. One of FeCrAl's superior mechanical properties is that it shows a linear curve representing elastic moduli as a function of temperature, which has been 220 GPa at 20 °C and reduced to 130 GPa at 1000 °C. By contrast, zircaloys show an ultimate strength (UTS) of 413 MPa, a yield strength (YS) of 241 MPa, and a 20% elongation break. Meanwhile, Kanthal remains constant between 400 and 500 °C, showing YS of 540 MPa and UTS of 740 MPa. Early, U$_3$Si$_2$/FeCrAl and U$_3$Si$_2$/SiC-SiC composite fuel-cladding systems have become promising ATF fuel systems.

RESULTS AND DISCUSSION

Consequently, UN-80%U$_3$Si$_2$-10% and 10% of porosity was the composite fuel, and ferritic (Kanthal APMT) was intended to replace zircaloys-4. The average temperature of the fuel and the release of UO$_2$ fission gas compared to silicide and nitride are shown in Figure 3, which shows fuel temperature and stack axial extension.
Another mechanical aspect of the fuel and cladding is present in the second phase. Nevertheless, the additional uranium density causes a slight drop in enrichment, which raises the neutron multiplication factor. The study concentrated on certain U-silicide phases because $U_3Si_5$ has a lower U-density and requires more enrichment to match the $^{235}U$-loading that can be achieved with $UO_2$. UN-$U_3Si_5$ with two volume contents of the UN phase, 55% and 80%, and 35% and 10% of the $U_3Si_5$ weight were examined using the ATF program. In the temperature range of steady-state operation, the thermal conductivity of pure UN-$U_3Si_2$ and UN-$U_3Si_5$ is approximately 5 to 7.5. For $UO_2$, UN-$U_3Si_5$, and UN-$U_3Si_5$, both display cycles of about 100 days. However, we used 10% of the weight of $U_3Si_5$. FRAPCON’s decreasing temperature of more than 250 °C should result in a modest release of fission gas and thermal expansion. According to the first post-irradiation evaluation, the UN-$U_3Si_2$ fuel system operated effectively at low burnup, causing minor pellet swelling and fission gas release (FGR). Figure 4 depicts FGR and fuel axial extension.

The UN-$U_3Si_5$ composite is a promising, more tolerant accident material for nuclear reactors that reacts to thermal neutrons, which is very similar to the $UO_2$ response. This exciting discovery suggests that it could easily switch from oxide operations to high-density ones, opening up new possibilities for its application.

When the UN and silicide phases come together, the thermal conductivity will increase, and the uranium loading will improve, making it even more helpful. In the UN-$U_3Si_5$ fuel concept, the $U_3Si_5$ phase must protect the nitride from water contaminants. The $U_3Si_2$, $U_3Si_5$, and UN are the best-mixed fuel options among the candidates. ATF fuel options have a high uranium density and good thermal conductivity.

The FeCrAl alloy and the SiC/SiC composite material are the most promising...
options for cladding because of their excellent strength and resistance to oxidation.

During a significant break-loss of coolant accident (LOCA), the FeCrAl cladding had meager oxidation and hydrogen production rates. However, $U_3Si_2$ can keep its crystal structure stable at 350 °C even when exposed to very high doses of radiation that cause amorphization (64 displacements per atom). The $U_3Si_2$ grain subdivision occurs at a relatively low dose. The higher pellet fuel thermal conductivity would reduce the stored thermal energy in the fuel, which is a critical factor during a LOCA.

Ferritic alloys produce a high neutron penalty, which results in a reduction in cladding thickness and an increase in pellet diameter. Thus, FeCrAl alloys use a cladding thickness of 0.0419 cm, while zircalloys use a thickness of 0.0572 cm. The fuel pellet exhibits an increased diameter of 0.4249 cm. Also, UN-$U_3Si$ has a low power density because it has a lot of heavy metals. It needs to be enriched with $^{235}U$ by 4.9% and $^{15}N$ by the same amount.

However, silicides like $U_3Si_5$ have significant effects. For example, they have a lower uranium density than $U_3Si$ and $U_3Si_2$. It has a higher melting point (1770 °C) than $U_3Si$ (925 °C) and $U_3Si_2$ (1665 °C). $U_3Si_5$ exhibits resistance to rapid oxidative pulverization at elevated temperatures. The starting temperatures for oxidation in $U_3Si_5$ and $U_3Si_2$ are about the same. However, the oxidation process in $U_3Si_5$ is faster, with a steeper slope of oxidative weight gain. Researchers in a different study found that the $U_3Si_5$ sample had microcracking, rapid oxidation, and a lower onset temperature than the $U_3Si_2$ and USi samples, which did not have microcracking as bad. This finding has significant implications for materials science and nuclear engineering.

**CONCLUSION**

The ATF idea shows a significant delay in fuel-cladding contact compared to traditional fuels of equal radial geometry and operational history. Sensitivity studies on fuel thermal creep rate, cladding thermal conductivity, cladding irradiation creep, cladding gap size, and cladding thickness indicate that research priorities for this concept in ATF should revolve around reducing cladding thickness, improving uranium densities and silicide-mixed nitride content, and increasing plasticity.

The goal is to verify the fuel’s mechanical and thermal properties under normal operating conditions. The tests conducted during the ATF program saw cycles of less than 20 GWD/tU. Still, we offer a simulation with a period of 2000 days. We modified the FRAPCON code to accommodate $U_3Si_5$ characteristics.

For PWRs, composite fuel based on UN, $U_3Si_2$, $U_3Si_5$, or $UB_2$ offers several benefits. Permitting greater burnup will enhance nuclear fuel performance, reduce waste quantities, and extend cycle times. UN-$U_3Si_5$ fuel has the following benefits: high uranium density, increased thermal conductivity, and reduced UN degradation in water contact. Instead, we will use the Kanthal APMT composition [Fe (Bal.) Cr (20–23%) Al (5.8%)] for zirconium alloys used as cladding. Nitride fuels will produce less stored energy if an accident occurs. Because Kanthal does not oxidize to form hydrogen, it is more resistant to coolant mishaps. It does not produce zirconium byproducts like hydrogen bursts.

**ACKNOWLEDGMENT**

The author thanks the Nuclear and Energy Research Institute (IPEN/CENEN/SP-Brazil) for providing these nuclear fuel investigations. The authors are grateful for IPEN’s technical assistance.
REFERENCE


