Substantiation of using uranium-zirconium carbonitride as kernel for microspherical fuel

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Abstract. The paper presents an alternative design of the micro fuel element with the use of a core made of uranium-zirconium carbonitride fuel instead of traditional uranium dioxide which has a detrimental effect on the micro fuel element operation due to oxygen. This fuel as part of the four-layer TRISO-micro fuel element creates significantly lower gas pressure under the coating, it is compatible well with a pyrocarbon coating and does not crack it. The fuel has high thermal properties and it is much less subject to the “amoeba”-effect.

1. Introduction

Safety assurance is one of the main tasks in development and operation of nuclear power plants. The accident events that occurred at Chernobyl and Fukushima nuclear power units have clearly demonstrate destructive properties of a steam-zirconium reaction occurred in severe accidents with loss of the coolant: when the required heat removal in the core is stopped for a long time, spontaneous heating of the nuclear fuel due to the decay heat leads to the fuel element destruction, hydrogen explosion and radioactive leak. These circumstances caused intensification of work on development of a fundamentally new fuel that is able to withstand severe accidents while maintaining or improving economic figures and safety during the normal operation. This fuel is called “Accident Tolerant Fuel” (ATF) - a fuel with increased accident resistance [1].

The basic requirements to the ATF fuel are:
- Safe behavior during the normal operation and under the conditions of design and beyond design basis accidents;
- Capability to operate sustainably in the nuclear reactor core in case of active cooling loss during the much longer period in comparison with the fuel available at the present time;
- Up-dated operational thermal and physical characteristics;
- Production processability;

It is obviously, the most reliable solution to eliminate the effect of the steam-zirconium reaction is to replace the basic structural material of the fuel element claddings - zirconium - with more inert one. Such material is graphite which is used in the concept of high-temperature gas-cooled reactors (HTGR) with helium coolant in domestic projects VGR-50, VG-400 and VGM. These reactors use the spherical micro fuel elements consisting of a miniature fuel core with a protective TRISO coating placed in the graphite matrix of free-lying ball fuel elements with a diameter of 60 mm or in the
prismatic fuel elements. However, there are a number of problems that impede development of this promising area of nuclear energy [2].

The object of this paper is to substantiate the use of the promising fuel type - uranium-zirconium carbonitride - as a core of spherical micro fuel elements instead of traditional uranium dioxide.

2. Statement of the problem

In 2014 the International scientific forum in the field of nuclear reactor development, Generation IV, assigned the status of HTGR type reactors as one of the six promising innovative projects of the 4th generation reactors [3]. The main advantages of HTGR reactors are:

- High efficiency up to ~ 48% at the coolant heating to the temperatures of ~ 1000° C;
- High level of fuel burnup up to ~ 80% FIMA;
- Use of spherical fuel micro particles with multilayer thermo- and radiation-resistant TRISO coatings, which allow the fission products to be effectively retained under all operating modes, including emergencies;
- Use of inert helium as a coolant with a low neutron capture cross section, that does not allow the coolant content in the reactor core to affect its reactivity;
- Universal modular design of the reactor, heat-resistant structural materials of the core and graphite-based reflectors, passive cooling system;
- A flexible fuel cycle allows the fuel based on U, Pu, Th, MOX to be used without changing the core design;
- Slight sensitivity to the equipment breakdowns.

The main drawback of HTGR reactors is a low power rating of the core during operation because of high safety requirements. In addition, a gas coolant has a low heat capacity; a long-lived β-active carbon ¹⁴C is formed in a large amount in the graphite moderator.

The operating conditions of the fuel elements in HTGR reactors are characterized by the following basic indicators [4]: irradiation time is 2-5 years, fast neutron fluence with an energy of E>0,18 MeV is about of (2-5)·10²¹ neutrons/cm², relative power is 2-6 kW/fuel element, maximal fuel temperature under the nominal mode is 1000-1300°C, fuel temperature under the emergency conditions is 1200-1600°C up to 10 hours. The ranges of the specified characteristics are connected with the difference in the reactor designs, their purpose and outlet temperature of the coolant. The operability of micro fuel elements in HTGR reactors is determined by a number of factors, including the microstructure and geometric parameters, chemical composition of the fuel core, and value of the initial free volume, etc.

The above-mentioned properties make it possible to use high-potential heat of HTGR reactors in different industries: power engineering, hydrogen production, chemistry, oil refining, metallurgy, etc.

The basic part of the fuel elements of HTGR reactor is micro-fuel elements - small spherical particles of the fuel core (kernel) with a protective multilayer TRISO-coating. A section of a typical micro fuel element with protective coatings is shown in figure 1. Micro fuel elements have a diameter of 200 to 1000 microns. Uranium dioxide enriched 5-20% is usually used as a fuel core. TRISO-coating is multilayer and consists of pyrolytic carbon (PyC) with different structure and density and silicon carbide (SiC). The cladding layers should provide a high level of the fission products retention within the micro fuel element. At present, the four-layer cladding design seems to be the most optimal.

The first layer, so-called buffer, is made of PyC pyrocarbon with a porosity of about 40-60%, and it is intended to protect the following dense PyC1 layer from the fission fragments influence. This layer to some extent compensates for bulk swelling of the fuel core. Along with the buffer layer porosity the free volume, accumulating gases, includes the core porosity and the gap between the core and cladding. The total free volume within the core with the buffer layer largely determines the allowable burnout of the fuel and its operating temperature.
The subsequent pyrocarbon layers (PyC1 and PyC3 in figure 1), as well as the high-density SiC layer, are power claddings that withstand the pressure of gaseous fission products (GPA) and also serve as diffusion barriers preventing the fission products from escaping out of micro fuel during their standard operation and under emergency situations.

A wide range of design, engineering, and material research, bench tests and reactor tests carried out in FSUE «LUCH» in the framework of micro fuel element development for domestic projects of HTGR reactors made it possible to significantly unify the micro fuel elements design (table 1) and ball uranium graphite fuel elements with a diameter of 60 mm based on them [5].

Table 1. Parameters and functions of micro fuel elements

| Layer No. | Material | h, μm | ρ, g/cm³ |
|-----------|----------|-------|----------|
| 1         | PyC      | 90    | ~1.0     |
| 2         | PyC1     | 60    | 1.8-1.9  |
| 3         | SiC      | 50    | 3.2      |
| 4         | PyC3     | 50    | 1.8-1.9  |

The developed physicochemical methods for spheroidization of the fuel cores - a thermoplastic slip method and sol-gel method based on the surface tension forces influence on a hardening drop, provided a density of at least 95% of the theoretical one: small deviations from the nominal diameter (500±50 μm) and aspheric coefficient of not more than 1.05.

The relative yield of such fission products out of the micro fuel elements at the fuel burning up of 10% and fast neutron fluence of $2\cdot10^{21}$ cm$^{-2}$ was not more than $10^{-5}$ under all temperature modes up to 1400°C. For the temperature ranges of 800-1100°C, which are the most typical for domestic HTGR reactor designs, the relative yield of fission products did not exceed $10^{-6}$-$10^{-7}$.

A partial yield of fission products from the VTGR micro fuel elements into the coolant is caused by the following:
- Contamination of the outer coatings of the micro fuel elements and graphite matrix with uranium in the process of manufacturing and operation;
- Micro fuel elements with defective coatings in the initial state are available or the micro fuel element coatings were destructed due to radiation-thermal processes and at the ultimate stress-strain state with subsequent evaporation of uranium;
- Diffusion of the fission products through coating layers.

Possible depressurization of the micro fuel elements and the fission products influx through the coatings become a controlling parameter for the fission products leakage during the operation process. The fuel and micro fuel element coatings are exposed to strong radiation exposure by the fission product fragments and neutrons during the operation. Bombardment by the fission fragments mainly affects the fuel parameters and nearby PyC buffer coating layer, which consequently undergoes shrinkage with subsequent exfoliation and cracking. Neutron irradiation is the main factor affecting the change in the properties of PyC1 and PyC3 and SiC power coatings. The physicochemical processes caused by high temperature and temperature fields variation occur in the micro fuel elements along with the radiation processes. Intense radiation thermal effects, as well as accumulation of GFP under the cladding cause changes in the stress-strain state of the coatings, which pressure level is determined by the released gas amount, core and buffer layer porosity, micro fuel element temperature and the fuel burnup depth. The pressure measurements under the cladding show that it reaches several hundreds of atmospheres, so the cladding acts as a pressure vessel. Growth of
processes of the fission product fragments radiation exposure on the coatings at irradiation, and chemical interaction of the coating materials, fuels, fission products and residual process gases, transfer of the solid fission products through the coatings, ultimate stress-strain state of the coatings can cause the micro fuel elements depressurization.

At the initial stage of burning up, when a portion of the damaged micro fuel elements is not more than 0.001%, the fission products release is determined by the contamination level of the outer cladding level and matrix graphite. At the next irradiation stages the fission products release is determined by the amount of the micro fuel elements with the damaged coating, and it can be up to 1% by the end of the operation. Therefore, the operational capability limit of the micro fuel elements is determined by the amount of the particles with the damaged coatings at the fabrication stage, and a rate of additional defects occurrence in the cause of life irradiation of the fuel.

During the burning-up process the UO₂ core undergoes significant structural changes: the element composition and oxygen potential are changed; the fuel is swollen about 1% for 1% of burning-up [6]. The oxygen released in the result of the fuel fission influences CO and CO² formation and the chemical composition of the fission products.

Besides it, when a temperature gradient is available, a typical grain excursion to the side of the hotter area is observed in the process of carbon re-condensation from the “hot” area of the coating to the “cold” one according to a scheme of 2CO↔C↓+CO², allowing the core to penetrate through the pyrocarbon coating layers up to the silicon carbide layer (figure 2a) and beyond its limits. This feature of the core behavior within the micro fuel element is called “amoeba”-effect [7].

At irradiating the PyC buffer layer structure undergoes a significant restructuring, and the area nearby the core is destroyed that causes the material shrinkage and compacting, occurrence of mechanical tension stresses, radial and tangential cracking of this layer. The radial cracks due to the proceeding shrinkage of the buffer layer fragments and interaction with oxygen released from the core, are transformed to the wide channels opening a direct access of the fission products to the inner dense pyrocarbon layer PyC1. After the crack passing through the PyC buffer and internal dense PyC1 pyrocarbon layers the crack is opened forming a through channel between the fuel core and SiC layer (figure 2b). Through this channel the fission products and released gases get a free access to the SiC layer causing its local corrosion specified by SiC+CO²→SiO²+2C reaction. The fuel penetration into the cracks of pyrolytic graphite layers can be noted.

**3. Solution of the problem**

The SiC layer is the basic power layer determining the micro fuel element efficiency. In-pile researches showed its high dimensional stability and small creep under irradiation in the range of the HTGR operational temperatures [8]. However, the effects described above and shown in Fig.2 have a negative effect on the SiC layer efficiency, and they are specified by the oxygen release intensity in the process of the fuel burning up. In contract to the oxide fuel, such fuel has much more content of fissionable isotope, better heat conductivity and, as a consequence much less temperature gradient, and also it keeps the structure stability during the operation [9]. This idea has been implemented in the conception of micro capsular fuel, where it is supposed to use the micro fuel elements in the matrix fuel element based on SiC [10].

The studies show that for the micro fuel with the core of the U(C,N) composition the “amoeba”-effect is negligible, and uranium-zirconium carbonitride fuel is practically free of this effect [11].
Besides it, (U,Zr)(C,N) does not cause significant gas pressures under the coating, has good compatibility with PyC and maximal thermal stability [12].

Table 2. Some comparative characteristics of different nuclear fuels [9]

| Characteristics                  | UO₂   | UN    | (U,Zr)C,N |
|----------------------------------|-------|-------|-----------|
| Uranium content, g/cm³           | 9.7   | 13.5  | 12.8      |
| Compression strength, σ, MPa     | 500   | 1950  | 1500      |
| Modulus of elasticity, E, MPa    | 180   | 210   | 280       |
| Coefficient of thermal conductivity, W/(m·K) | 8    | 26    | 32        |
| Vapor pressure at 1800°C mPa     | 130   | 27    | 4         |
| Volume swelling, % burn up (at 1700°C) | 3.0-6.0 | 0.6-1.5 | 0.8-2.0 |

Comparison of different fuel types characteristics show that (U,Zr)C,N exceeds uranium dioxide by all thermophysical parameters (table 2). This fuel is a modification of the nitride fuel: at the uranium density less only by 10% it significantly increases thermal conductivity and operational temperature up to 2600°C, its saturated steam pressure is significantly less (figure 3), it increases in stability at emergency overheating – a period of time until melting is by 3 times more than uranium nitride, and by 4 times more than uranium dioxide has.

![Figure 3. Temperature effect on oxygen pressure over uranium dioxide (a), nitrogen pressure over uranium nitride (b) and over uranium-zirconium carbonitride (c) [9].](image)

The presented arguments will give rise to consider uranium-zirconium carbonitride fuel as advanced one for use in the spherical micro fuel of HTGR reactors which allows the operational characteristics to be improved besides a decision of basic problems of the fuel and covering compatibility.

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