Technologies for manufacturing UO$_2$ sintered pellets to fuel burnup extension

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Abstract

The actual tendency all over the world is to manufacture fuel bundles capable to resist high burn-up. The factors affecting the burn-up increase are: the pellet-cladding mechanical interaction (PCMI), the oxidation and hydriding of the Zircaloy-4 sheath, the increase of internal pressure, stress corrosion cracking, Zircaloy-4 irradiation growth, fuel swelling. A way to increase fuel burn-up is to diminish the elements internal pressure by adequate UO$_2$ fuel pellet structure (large grain or controlled closed porosity). In the large grain size UO$_2$ pellets, fission gas release rate decreases and the elements internal pressure increase slowly. Similarly, in the UO$_2$ sintered pellet with controlled closed porosity the fission gas accommodation is better and the elements internal pressure increases slowly. The paper presents a literature review related to the technologies and the methods for manufacturing UO$_2$ sintered pellets to fuel burnup extension. The flowsheets for large grains and controlled closed porosity UO$_2$ sintered pellets obtained by Nb$_2$O$_5$ dopant respectively pores former addition in UO$_2$ sinterable powder, pressing and sintering in H$_2$ atmosphere are exposed. In the diagrams are presented the dependency of the main sintered pellet characteristics (pore radius distribution, pores volume, density, grains size) as function of the Nb$_2$O$_5$ dopant concentration, UO$_2$ sinterable powder nature and sintering temperature. Other sintered pellets characteristics (electrical conductivity, Seebeck coefficient, high temperature molar heat capacity and thermomechanical properties) are presented. The technologies for sintered pellets manufacturing for RU, DUPIC, MOX fuel cycles are presented. A proposal related to fuel manufacturing from Uranium compound resulted in LWR spent fuel reprocessing is also given.

1. INTRODUCTION

A main concern all over the world is to increase fuel burn-up for reducing nuclear electricity costs and the high level waste (spend fuel) amount. Very good results were obtained in the removing or the diminishing of the factors affecting the burn-up increase and the theoretical and practical (experimental results) solutions proposed to diminish adverse effects.

Table 1 presents some factors affecting the burn-up increase and the solutions.

A way to increase fuel burn-up is to diminish the elements internal pressure by adequate UO$_2$ fuel pellet structure (large grain or controlled closed porosity). In the large grain size UO$_2$ pellets, fission gas release rate decreases and the elements internal pressure increases slowly. Similarly, in the UO$_2$ sintered pellet with controlled closed porosity the fission gas accommodation is better and the elements internal pressure increases slowly.
Table 1. Factors affecting burnup increase

<table>
<thead>
<tr>
<th>Factor</th>
<th>Solutions</th>
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<tr>
<td>Increasing of internal temperature</td>
<td>- reducing of elements diameter [1]</td>
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<tr>
<td></td>
<td>- pellets with central hole [2]</td>
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<td></td>
<td>- duplex pellets [3]</td>
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<td></td>
<td>- graphite discs between pellets [4-5]</td>
</tr>
<tr>
<td>increasing of internal pressure</td>
<td>- large grain size pellets [6-8]</td>
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<tr>
<td></td>
<td>- controlled closed porosity</td>
</tr>
<tr>
<td>pellet-cladding mechanical interaction (PCMI)</td>
<td>- pellet length/diameter &lt; 1 [9]</td>
</tr>
<tr>
<td></td>
<td>- pellet geometry improvement [10]</td>
</tr>
<tr>
<td>stress corrosion cracking</td>
<td>- Zy-4 sheath covered with pure Zr [11]</td>
</tr>
<tr>
<td>oxidation and hydriding of the Zircaloy-4 sheath</td>
<td>- new microstructure for Zy-4 [12]</td>
</tr>
<tr>
<td></td>
<td>- new Zr alloys (ZIRLO- Nb1%, Sn1% and Fe 0.1%) [13]</td>
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Other way to reduce fission gas release rate is to use composite fuels. Two type of disperse fuels for water reactors are known:

- **ceramic – metallic** (cermet) where inert matrix are metals (Zr, Al, Mo) and ceramic fissile materials ($^{235}$U and Pu compounds with O2, Si, C);

- **ceramic – ceramic** (cercer) where inert matrix may be ceramics (MgO, MgAl$_2$O$_4$) and the ceramic fissile materials are the same like cerments.

The increasing of internal temperature appears because the fuel thermal conductivity decreases with the burn-up and heat removing is worsened. The solutions are reducing of element diameter [1], pellets with central hole [2], duplex pellets [3], graphite discs between pellets [4-5] and others.

Some solutions proposed for pellet cladding mechanical interaction (PCMI) reduction are pellet length/diameter < 1 [9], pellet geometry optimization [10].

The internal and external corrosion issue are resolved by Zy-4 sheath covered with pure Zr [11], new microstructure for Zy-4 [12], new Zr alloys (ZIRLO- Nb1%, Sn1% and Fe 0.1%) [13].

The RU, DUPIC, MOX fuel cycles and CANFLEX fuel type concept are modern ways to extend burn-up. Much solution for burn-up extension bad effects removing, presented above, retrieves in these modalities.
2. TECHNOLOGIES FOR UO₂ LARGE GRAINS MANUFACTURING

One of the ways to increase pellets grain size without increasing sintering temperature and time is the addition of small quantities (< 1% wt M/U) of sintering additives (aliovalent metal or rare earth oxide).

By the addition of certain dopants in the UO₂ powder (TiO₂, Nb₂O₅, Cr₂O₃, CaO, V₂O₅) the grain size, porosity and the mean free diffusion path are increased, whereas the grain boundary area is reduced [14–18].

At the Institute for Nuclear Research (ICN) - Pitesti a technology for obtaining large grains size UO₂ pellets using dopants [19] was developed. The manufacturing flowsheet is presented in Figure 1.

![Figure 1. Large grain size sintered pellets manufacturing flowsheet](image-url)
The UO₂ non-free flowing powder, manufactured by ADU route, was mixed with Nb₂O₅ in an Y - con master mix. The blended powder was pre-pressed and granulated using a 0.5 mm sieve. The resulted granules were mixed with Zn stearate as lubricant. The green pellets were manufactured by bilateral pressing. The compacts were directly sintered (4 hours at 1700°C) in standard continuous sintering furnace with a dewaxing step at 900°C.

For the production of niobia doped UO₂ fuel the “direct pelletizing process” which has been developed in relation with the AUC powder technology can be applied without any change beside the admixture of niobia to the UO₂ powder.

In a master mix UO₂ and Nb₂O₅ powders are added and homogenized. The blended powder is directly pressed without the addition of a lubricant. The green pellets are sintered in a sintering furnace. Under the same sintering conditions, the density of the pellets can be adjusted by U₃O₈ addition, UO₂ - Nb₂O₅ pellets with densities between 9.9 - 10.75 g/cm³ and grain size between 2 - 50 μm being obtained [20].

Other methods to obtain uranium dioxide pellets with large grain sizes are:

- heating sintered pellet of uranium dioxide at temperatures higher than 1700°C in hydrogen stream containing silicate vapors, resulting from the aluminum silicate decomposition. The grain size values can be increased to more than 50μm [21];

- production of sintered uranium dioxide pellets by the addition of sintering agent (10 - 55wt% MgO and 90 - 45wt%SiO₂) or precursor thereof in the composition ranging from 0.1 - 0.8wt% of a sinterable mixture. The resulting mixture is turned into a compact. The sintering process is performed at a temperature where the sintering agent forms a liquid phase to produce a sintered product. The precursor is thermally decomposed below the sintering temperature [22];

- obtaining of sintered UO₂ nuclear fuel pellets, with the average grain size ranging from about 30μm to about 80μm by the addition of magnesium aluminosilicate in uranium dioxide powder. The pores volume is ranging between 2 and 10% [23];

- addition of Cr₂O₃ or Al₂O₃ and of small quantities of SiO₂ into the uranium dioxide powder [24].

The physical, thermal, electrical and mechanical properties of Nb₂O₅ - doped UO₂ pellets are affected, as compared to the undoped ones.

The variation in density of Nb₂O₅ - doped UO₂ pellets as a function of Nb content is presented in Figure 2. A very small concentration of Nb₂O₅ (0-0.1%Nb/U) leads to a minimum value of the UO₂ pellet density. The density of UO₂ pellets increases with the increase of the Nb content for low concentrations (0.1 0.2% Nb/U). At concentrations higher than 0.2%Nb/U, the density values are different, depending on the manufacturing routes; the increase of the Nb content slowly diminishes the density (P₁ -ADU route) or remains constant (P₂ - IDR route). Figure 3 displays the grain size dependence of the UO₂ pellets on the Nb content [19]. The dopant addition determines a significant grain growth. The average grain size, versus concentration, shows an increase up to a maximum value (0.5%) followed by a constant value.
Figure 2. Density of sintered pellets versus Nb concentration

Figure 3. Grain size dependence versus Nb concentration
The addition of dopant brings changes into the porosity of sintered pellets. The total pores volume evolution versus Nb concentration in Nb₂O₅ - doped UO₂ sintered pellets is presented in Figure 4 [19].

At low Nb concentrations the pores volume is distributed in small pores. If the Nb concentration increases, the pores volume is distributed in large pores, that prevail, while small pores volume is negligible [19].

Nb addition affects the UO₂ pellets mechanical properties [19], [25] as shown in Figure 5.

The transgranular fracture observed at low temperature (≤400°C) points out the intense cohesion between the grains. If the temperature increases the intergranular fracture is dominant and only this type of rupture takes place at high temperature (≥ 850°C), Figure 6.

The electrical conductivity and Seebeck coefficient of Nb₂O₅ - doped UO₂ have been measured and compared with undoped UO₂. Niobium acts as a donor impurity in UO₂, but is not completely ionized and does not lead to n-type extrinsic behavior. On the contrary, intrinsic conductivity is observed and this is attributed to Nb compensating for acceptor levels due to slight excess oxygen nearly stoechiometric UO₂. The value of the band gap in UO₂ is measured to be 2.14eV for undoped material and 2.26 eV for doped UO₂ [26].

High temperature molar heat capacity of Nb₂O₅ - doped UO₂ are practically the same as that of UO₂, [27].
Figure 5. Diametral compressive strength

Figure 6. Intergranular fracture
3. OBTAINING OF UO₂ SINTERED PELLETS WITH CONTROLLED POROSITY

The technology for manufacturing of UO₂ sintered pellets with controlled porosity is relatively simple using pores former. UO₂ sinterable powder is mixed with pores former and thereafter the sintered pellets are elaborated by usually methods.

The common pores former can be organic compounds, UO₂ powder precursors (ADU, UO₃, U₃O₈) or powder resulted from sintered pellets calcination.

In the Figure 7 [28] is presented a flowchart for UO₂ sintered pellets with controlled porosity, manufactured from no free flowing UO₂ sinterable powder.

The powder homogenization is very important to obtain uniform porosity. If the mix powder – pores former is non-adequate it appears connected pores and grouping porosity. Therefore, the first step is to make a preliminary admixing of pores former with about 10%wt of batch powder and thereafter this is mixed with the rest. The manufacturing is continued with compacts pre-pressing and granulation, granule homogenization with Zinc stearate, green pellets pressing and sintering in hydrogen atmosphere. The sintered pellets are grinded in a centerless grinding machine. The washing, the drying and the quality control of the grinded pellets are the last steps in the obtaining process.

The pores structure and volume are dependent on pore former amount, pre-pressing and pressing pressure and thermal treatment conditions. If the technical conditions will be well selected, desired microstructure will be obtained.

UO₂ sintered pellets with homogenous controlled porosity can be obtained directly from the UO₂ powder. UO₂ sinterable powder thermal is treated (few hours) in hydrogen above the reduction temperature and thereafter the sintered pellets are manufactured by usual way. Desired pores structure and volume are obtained in terms of the technical conditions.

4. UO₂ PELLETS MANUFACTURING FROM RECOVERED URANIUM

Recovered Uranium (RU) resulted like by-product from conventional reprocessing of LWR spent fuel for Pu obtaining. The enrichment of RU is about 0.9% U²³⁵ and it contain Uranium daughter products and traces of transuranic elements [29] (Table 2).

Table 2. Uranium daughters and transuranic elements in RU.

<table>
<thead>
<tr>
<th>U daughters</th>
<th>Contents</th>
<th>U₉₅₅</th>
<th>Nuclide</th>
<th>Range g/gU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U²³²</td>
<td>0.15 - 1 ppb</td>
<td>0.0055%</td>
<td>Np</td>
<td>3.10⁻⁶</td>
</tr>
<tr>
<td>U²³⁴</td>
<td>0.014 - 0.018%</td>
<td></td>
<td>Pu</td>
<td>3.10⁻⁵</td>
</tr>
<tr>
<td>U²³⁵</td>
<td>0.85 - 0.95%</td>
<td>0.711%</td>
<td>Am</td>
<td>1.10⁻⁸</td>
</tr>
<tr>
<td>U²³⁶</td>
<td>0.28 - 0.4%</td>
<td></td>
<td>Cm</td>
<td>1.10⁻⁹</td>
</tr>
<tr>
<td>U²³⁸</td>
<td>98.856 - 98.632</td>
<td>99.289</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7. Controlled porosity sintered pellets manufacturing flowsheet
The quantity of RU in Europe and Japan is about 25,000 t [29].

RU resulted from reprocessing is Uranium Nitrate (UN). UN is converted in UO₃ by denitration (BNFL) or in U₃O₈ by ADU route (COGEMA). The manufacturing of UO₂ pellets is usually. UO₂ powder is manufactured by reduction of UO₃ or U₃O₈ with hydrogen. If UO₃ is converted to UF₆ (for enrichment), the Integrated Dry Route (IDR) is applicable. UO₂ sintered pellets can be manufactured anywhere it exists facilities, devices and technologies for UO₂ no free flowing powder manufacturing (Figure 8).
The difference between powder and pellets manufacturing from natural uranium and RU is the radiological inventory of RU, dependent of the fuel history (reprocessing, aging stage, burnup). In every process, volatile fission product can be released. That imposes supplementary measures for operators and environment protection. During sintering the release of $^{137}\text{Cs}$ and other volatile products was detected. But AECL concludes that no significant radiological field in a commercial fuel manufacturing plant would build up due to release of volatile products.

An international collaboration between Korea Atomic Energy Research Institute (KAERI), Atomic Energy of Canada Limited (AECL) and British Nuclear Fuel plc (BNFL) to use RU was developed. KAERI and AECL have introduced the Canadian Flexible (CANFLEX) fuel concept as a vehicle for this fuel cycle. A very attractive alternative to use RU in CANDU Reactors appears. Theoretically [29] the quantity of 25,000 t of RU would provide sufficient fuel for 500 CANDU reactor years of operation, knowing that the annual refuelling requirement for a RU fuel burnup 13 MWd/KgU is around 50 t/an comparatively with 85 t/an for NU.

5. SINTERED PELLETS FABRICATION FOR DUPIC [30-32]

The DUPIC (Direct Use for spent PWR fuel in CANDU) is the fuel cycle where the spent PWR fuel is dry processed into CANFLEX fuel for the additional burnup of about 15 MWd/KgUHE (Heavy Element) in CANDU Reactor. AECL, KAERI, USDOE and USDOS proposed the DUPIC fuel cycle concept. The PWR spent fuel, having a nominal burnup of 35 MWd/KUHE contain 0.9wt% fissile uranium and 0.6wt% fissile plutonium, more then natural uranium with 0.711wt% fissile content. UO$_2$ powder, from PWR spent fuel manufacturing is based on OREOX (Oxidation Reduction of Oxide Fuel) process (Figure 9). When UO$_2$ is oxidized to U$_3$O$_8$, the crystallographic system is changed elemental cell volume increase, the stresses appear and pellets are broken themselves. The process is repeated to obtain a very fine powder.

The powder resulted from OREOX process is conditioned by milling to increase the sinterability. The sinterable powder is pressed into pellets and green pellets are sintered to 95 - 98 % TD (Theoretical Density). The sintered pellets are grounded on centerless grinding machine (dry process only) to final diameter and surface.

The DUPIC being a dry processing technology to manufacture CANDU fuel from PWR spent fuel without separating fissile materials and stable fission products from the spent fuel needs experimental works to verify the performance. In Korea, the simulated sintered pellet where manufactured, the irradiation testing program will be started in 2000.

6. MOX SINTERED PELLETS MANUFACTURING

The MIMAS (MIcronized MAster blend) process for MOX fuel obtaining (for LWRs) was developed by BelgoNucleaire (BN) in the Dessel plant. The MIMAS MOX pellets are a solid solution of UO$_2$ and PuO$_2$, homogeneously dispersed in a UO$_2$ matrix [33]. Schematically the process is presented in the Figure 11.
Figure 9. OREOX Process

Figure 10. DUPIC process
The powder preparation has two blending steps: the primary (master) blend obtained by ball milling (micronization) and secondary (final) blend. The powder obtained is pelletized. The green pellets are sintered in H2/Ar atmosphere and the sintered pellets are dry grinded.

The MIMAS process can lead to excellent isotopic homogeneity of the Pu in the product even with Pu of various origins, forms and batch sizes because it has double blending.

A way to manufacture MOX fuel (for FBRs) is the microsphere obtaining and densification by vibro-compacting [34].

The concentrated solution of U and Pu nitrate mixed with the organic gelling agent is added in ammonia like small drops. The obtained microsphere are washed in water, dried, calcinated and sintered. The pin is filled with sintered microsphere by vibrocompacting.

In Canada, AECL MOX fuel fabrication activities are conducted in the Recycle Fuel Fabrication Laboratories (RFFL). The RFFL fabrication process [35] is presented in Figure 12.
The process consists in blending of UO₂ and PuO₂ powders in Master-Mix blend followed by usual manufacturing of sintered pellets from no free flowing powder. Therefore, the powder is pre-pressed and obtained compacts are granulated. The granulation process is necessary to adapt the powder flowability for transport and filling of the pressing tools. The granules are pressed and green pellets are sintered in hydrogen atmosphere. The sintered pellets are grinded in a centerless grinding machine.

The Indian option for MOX sintered pellets manufacturing is approximately the same [36].

7. PROPOSAL FOR FUEL MANUFACTURING FROM RU

For CANDU owners, the utilization of fuel based on the RU way seems to be very attractive particularly having in view the shorten time necessary to develop adequate manufacturing
processes to perform suitable tests. Romania is interested to enlarge the existing R & D activities in this field.

Romania have some important facilities necessaries for the fuel development, such as:

- Nuclear fuel plant;
- TRIGA reactor (14 MW) for materials testing;
- Post-irradiation laboratories;
- Out of pile facilities;
- Competence and experience in CANDU fuel type manufacturing.

We are open for a co-operation in order to obtain all the information needed for industrial implementation.

8. CONCLUSIONS

In the nuclear word, many efforts for fuel manufacturing resistant to extended burn-up were make. Many new technology offer the possibility to use the available manufacturing equipment and quality assurance programs from commercial production without specially modifications. The technologies for extended burn-up fuel manufacturing are available. The main direction in this field will be to adapt the existent facilities for this reason.

Increasing burn-up, which allows the utility to get the same kWh output with a reduced amount of higher enriched fissile material, provides a saving not only in the cost of fuel fabrication but also in the cost of disposal of the irradiated fuel. This latter cost is two to four times higher than that of fuel fabrication. Reducing the quantity of irradiated fuel also has a positive impact on the environmentally acceptable solution adopted for its disposal.

This is true not only for fresh uranium fuel, but also for mixed oxide (MOX) fuel. For MOX fuel, the goal is to achieve the same higher burnups as with uranium fuel. Higher burnups make MOX fuel more competitive in comparison with fresh uranium fuel, because the latter requires more uranium feed and enrichment to achieve higher burnups. Meanwhile, the safety authorities are increasing their requirements to license higher burnup fuels, asking for more representative material tests under accidental conditions, more feedback from experience and testing, before granting a license.

REFERENCES


