Test Results of PBMR Fuel Spheres

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Abstract – Results of pre-irradiation testing of fuel spheres (FS) and coated particles (CP) manufactured by PBMR SOC (Republic of South Africa) are described. The stable high quality level of major characteristics (dimensions, CP coating structure, uranium-235 contamination of the FS matrix graphite and the outer PyC layer of the CP coating) are shown. Results of a methodical irradiation test of two FS in helium and neon medium at temperatures of 800 to 1300 °C with simultaneous determination of release-to-birth ratios for major gaseous fission products (GFP) are described.

I. INTRODUCTION

Before irradiation testing and following post-irradiation examination (PIE) of FS, it is very important to obtain comprehensive information about:

– initial characteristics of FS and CP;
– experimental verification of reaching temperature and neutronic irradiation targets for irradiation of FS;
– experimental evaluation of limiting sources of fission products (FP) in FS structural elements namely: matrix graphite (MG), CP coating, and fuel kernel.

The authors place high emphasis on the latter (the behavior of FP) taking into account their technical approach for HTR fuel qualification [1].

II. PRE-IRRADIATION TESTING OF FUEL SPHERES

Sixteen PBMR pre-production fuel spheres of lot FSA-J01 (PBMR-certified values: diameter of 60 mm, fuel-free zone thickness of 6.6 mm, uranium mass of 9 g with U-235 enrichment of 9.6% each) were delivered to the Joint-Stock Company “Institute of Nuclear Materials” (JSC “INM”) in September 2009.

II.A. FS Diameter Measurements

FS diameters were measured by a micrometer of Mitutoyo Co. (Japan) mounted so that its measurement axis was in a FS diametral plane. The measurement uncertainty was ±0.001 mm. Each FS was measured thrice in six planes (with a step of about 60°) parallel (D1) and transverse (D2) to the FS pressing axis. The measurement results of FS diameters are given in Fig.1.

The FS diameters are scattered from 59.78 to 59.98 mm at that the mean diameter $D_1$ is about 0.35% higher than $D_2$.

II.B. Determination of Uranium-235 Concentration in Matrix Graphite of Fuel Spheres

Deconsolidation of two FS Nos. G01 and G17 were performed with traceable removal of deconsolidation components from an electrolytic bath [2] in order to determine the uranium 235 (U-235) concentration in the matrix graphite (MG).

A FS was deconsolidated in two stages:

• radial deconsolidation (Fig.2) to obtain a cylinder of diameter about 23 mm, followed by
• axial deconsolidation (Fig.3) in several steps to obtain samples of deconsolidation components (etched and washing solutions, MG powder, and CP).

CP were separated from MG powder, dried, and weighted. Radial CP density in the FS fuel zone varies within limits of about 25% (Fig.4). This guarantees the absence of localized overheating in the FS fuel zone.
The U-235 concentration in the MG powder was determined by short irradiation of a sample and measuring its Np-239 content by means of gamma spectrometry.

The U-235 mass contained in the $i$ th sample of MG after the appropriate axial deconsolidation step, $m_{U5,i}^{pr}$ (g $^{235}$U), was calculated by the formula

$$m_{U5,i}^{pr} = m_{MG,i}^{pr} \times \frac{w_{U5}^{sp}}{100\% - w_{U5}^{sp}} \times \frac{A_{U,Np,i}^{sp} \cdot t_{irr,i}^{sp} \cdot \frac{N_{U,i}^{sp} \cdot M_{U}}{N_A} \cdot 100\% - w_{U5}^{ut}}{A_{U,Np}^{sp} \cdot t_{irr,i}^{ut} \cdot \frac{N_{U,i}^{ut} \cdot M_{U}}{N_A} \cdot 100\%}$$

where

$m_{MG,i}^{pr}$ = mass of MG powder generated during the $i$ th step of the FS deconsolidation (g),

$m_{MG,i}^{sp}$ = mass of the $i$ th MG sample taken from the MG powder generated during the $i$ th step of FS deconsolidation (g),

$w_{U5}^{sp}$ = U-235 enrichment of uranium in the MG samples (mass %) [$w_{U5}^{sp} = 9.6\%$ (the certified value for PBMR FS)],

$w_{U5}^{ut}$ = U-235 enrichment in the standard uranium sample (mass %) [$w_{U5}^{ut} = 0.72\%$ (natural uranium)],

$A_{0,Np,i}^{sp}$ = decay-corrected Np-239 activity in the $i$ th MG sample (Ci),

$A_{0,Np}^{ut}$ = decay-corrected Np-239 activity in the standard uranium sample (Ci),

$t_{irr,i}^{ut}$ = irradiation time (days) for the standard uranium sample,

$t_{irr,i}^{sp}$ = irradiation time (days) for the $i$ th MG sample,

$N_{U,i}^{ut}$ = the certified number of U-235 atoms in an appropriate standard uranium sample: $N_{U,i}^{ut} = 2.08E+17$ atoms $^{235}$U ($\pm 5\%$ at $P=0.95$),

$N_{U,i}^{ut} = 1.88E+17$ atoms $^{235}$U ($\pm 5\%$ at $P=0.95$),

$N_A = 6.022 \times 10^{23}$ mol$^{-1}$ (Avogadro number);

$M_{U} = 238.03$ g/mol (molar mass of natural uranium).

Liquid deconsolidation components for each deconsolidation step were combined and the U-235 concentration in a sample was determined by alpha-radiography with plastic track detectors (PTD) [3].

A typical appearance of a PTD is shown in Fig. 5.
taken from the total solution generated during the i th step of the FS disintegration (g 235U/ml).

\[ C_{US,b} = \text{background U-235 concentration determined in a blank aliquot (g 235U/ml)} \]

\[ V_{tot,i} = \text{volume of total solution of spent electrolyte and washing waters generated after the i th step of the FS deconsolidation (ml)} \]

The U-235 concentration in the i th part of MG deconsolidated from an appropriate FS, \( C_{US,i}^{MG} \) (atoms 235U/g MG), was calculated by the formula:

\[ C_{US,i}^{MG} = \frac{m_{US,i}^{w} + m_{US,i}^{b}}{m_{MG,i}^{w}} \cdot \rho_{MG} \cdot \frac{N_{A}}{M_{US}} \]

where

\[ \rho_{MG} = 1.75 \text{ g/cm}^3 \] (the certified density of the PBMR matrix graphite),

\[ N_{A} = 6.022 \times 10^{23} \text{ atom/mol (Avogadro number)} \]

\[ M_{US} = 235 \text{ g/mol (U-235 molar mass)} \]

Finally, the U-235 concentration in the FS matrix graphite was (at \( P = 0.95 \)):

\( (1.2 \pm 0.5) \times 10^{13} \) atom 235U/cm3 MG for FS G01,

\( (1.4 \pm 0.2) \times 10^{13} \) atom 235U/cm3 MG for FS G17.

This was about \( 1.5 \times 10^{-9} \) of the U-235 concentration in a PBMR kernel and was evidence of the absence of initial through-coating cracks in CP. The evaluated ratio of total U-235 in the matrix to that in the fuel particles for the entire sphere is about \( 6 \times 10^{-7} \).

II.C. Determination of Uranium-235 Concentration in Outer PyC Layer of Coated Particles

At first, each CP lot (a fraction of the total number of CP deconsolidated from the appropriate FS G01 or G17) was weighed and subjected to acid treatment twice followed by chemical etching in four steps. On completion each etching step, the etched solution and washing water were separated from the CP (Fig.6). The CP were dried and weighed.

Fig. 6: Appearance of CP before (a) and after (b) etching of oPyC layer.

After each etching step, etch and washing solutions were combined into a single volume from which an aliquot of 25 ml was sampled. CP were dried and weighed. The etched thickness of the oPyC layer, \( \delta_{i} \) (mm), was calculated by the formula

\[ \delta_{i} = \frac{D_{i-1} - D_{i}}{2} \]

where

\[ D_{i} = \left( D_{i-1}^{3} - \frac{6 \cdot (m_{i} - m_{i-1})}{\pi \cdot \rho \cdot k} \right)^{1/3} \]

\[ D_{i-1} = \text{CP diameter at beginning of the i th etching step (cm)} \]

\[ m_{i} = \text{mass of CP lot on completion of the i th etching step (g)} \]

\[ m_{i-1} = \text{mass of CP lot at the beginning of the i th etching step (g)} \]

\[ \rho = 1.93 \text{ g/cm}^3 \] (PBMR-certified density of the oPyC layer),

\[ k = \text{the calculated number of CP in the lot} \]

\[ k = m_{0}/m_{CP} \]

\[ m_{0} = \text{initial mass of the CP lot (g)} \]

\[ m_{CP} = 0.0013712 \text{ g (PBMR-certified mass of one coated particle)} \]

\[ k = 5.0387 / 0.0013712 = 3675 \]

\[ k = 5.0762 / 0.0013712 = 3702 \]

The 25-ml liquid blank sample of distillated water, 25-ml standard samples of natural uranium, and 25-ml liquid aliquots of total (etched and washing) solutions were irradiated for a short time together with plastic track detectors and standard scandium-45 samples.

On completion of irradiation and required cooling time, the following was performed:

a) gamma spectrometry of scandium standard samples (Sc-46) to determine thermal neutron fluence and irradiation irregularity through the samples,

b) chemical treatment of plastic track detectors and determination of U-235 concentration in the 25-ml liquid aliquots and liquid standard samples[3].

The U-235 mass released into the acid solution during the double acid treatment of the appropriate CP lot, \( m_{US,i}^{as} \) (g 235U), was calculated by the formula

\[ m_{US,i}^{as} = (1.3 C_{US,i}^{as} - 0.7 C_{US,b}^{as}) \cdot V_{tot,i} \]

for \( 0.7 C_{US,b}^{as} < 1.3 C_{US,i}^{as} \), and

\[ m_{US,i}^{as} = (C_{US,i}^{as} - C_{US,b}^{as}) \cdot V_{tot,i} \]

otherwise

\[ C_{US,b}^{as} = \text{U-235 concentration in a 25-ml aliquot taken from the solution formed during the acid treatment of the appropriate CP lot (g 235U/ml)} \]

\[ C_{US,b}^{as} = 3.2 \times 10^{-12} \text{ g 235U/ml (background U-235 concentration in a blank acid sample determined with a standard uncertainty of } \pm 15\% \),
The $V_{\text{tot},i}$ volume of the acid solution after the double acid treatment (ml).

The U-235 mass released into the etched solution during the $i$ th oPyC etching step of the appropriate CP lot, $m_{U5,i}^{es}$ (g $^{235}$U), was calculated by the formula

$$m_{U5,i}^{es} = (1.3C_{U5,i}^{es} - 0.7C_{U5,b}^{es}) \cdot V_{\text{tot},i}$$

for $0.7C_{U5,b}^{es} < 1.3C_{U5,i}^{es}$, and

$$m_{U5,i}^{es} = (C_{U5,i}^{es} - C_{U5,b}^{es}) \cdot V_{\text{tot},i}$$

otherwise

where

$C_{U5,i}^{es}$ = U-235 concentration in a 25-ml aliquot taken from the total (etching and washing) solution formed during the $i$ th oPyC etching step of the appropriate CP lot (g $^{235}$U/ml),

$C_{U5,b}^{es}$ = $6.0 \times 10^{-12}$ g $^{235}$U/ml (background U-235 concentration in a blank etching sample determined with a standard uncertainty of ±15%),

$V_{\text{tot},i}$ = volume of the total solution (etched solution and washing water) on completion of the $i$ th etching step (ml).

The U-235 concentration in the $i$ th part of the etched oPyC layer, $C_{U5,i}^{oPyC}$ ($^{235}$U atoms/cm$^3$ oPyC), was calculated by the formula

$$C_{U5,i}^{oPyC} = \frac{m_{U5,i}^{es}}{m_{oPyC,i}^{es} \cdot \rho_{oPyC} \cdot N_A \cdot M_{U5}}$$

where

$\rho_{oPyC}$ = 1.93 g/cm$^3$ (PBMR-certified density of the oPyC layer),

$m_{U5,i}^{es}$ = U-235 mass in the total solutions generated in the $i$ th etching step (g $^{235}$U),

$m_{oPyC,i}^{es}$ = oPyC mass etched in the $i$ th step (g),

$N_A$ = $6.022 \times 10^{23}$ mol$^{-1}$ (Avogadro number),

$M_{U5}$ = 235 g/mol (U-235 molar mass).

Finally, the U-235 concentration in the oPyC layer was (at $P = 0.95$):

$(1.8 \pm 0.4) \times 10^{13}$ atom $^{235}$U/cm$^3$ oPyC FS G01,

$(2.1 \pm 0.4) \times 10^{13}$ atom $^{235}$U/cm$^3$ oPyC FS G17.

Measured U-235 profiles in oPyC and MG of FS are shown in Fig.7.

**II.D. Ceramography of Coated Particles**

Ceramography of CP deconsolidated from FS G01 and G17 (Fig.8) showed that:

1) No influence of deconsolidation process on the CP coating structure was observed.

2) All four CP coating layers (outer dense PyC, SiC, inner dense PyC, and buffer carbon layers) were in good condition. No cracks in the layers and gaps between the layers were observed.

3) SiC layers on most of the CP appeared homogeneous and dense, without visible pores and foreign phases.

![Fig. 7: U-235 profile in FS structural components.](image_url)

![Fig. 8: Stucture of CP deconsolidated from FS G01.](image_url)
III. METHODICAL REACTOR TEST OF FUEL SPHERES

Methodical reactor testing of two PBMR pre-production fuel spheres G08 and G41 was performed from 11 Nov 2009 to 11 Dec 2009. Each FS was placed in a capsule (Fig.9) containing two steel cases and a graphite cup. The graphite cup was separated from the internal case by means of graphite fins.

Nicrosil-nisil thermocouples were installed in bores of the upper graphite cup and on the inner surface of the internal steel case. The capsules were purged in turn using the Gas Handling System “RISK” in order to sample GFP from the working gap of an appropriate capsule for gamma spectrometry.

One bare PBMR kernel (0.65±0.03 mg UO2 [at $P=0.95]$ of 9.6% enrichment in U$-^{235}$) was used to examine GFP release from a FS with a single initially failed CP during the first hours of irradiation when the kernel structure is still unchanged due to irradiation and accumulation of GFP in kernel pores.

During irradiation the graphite cup temperature ($T_G, °C$) was measured, and the FS center temperature ($T_F, °C$) was calculated using the values $T_G (°C)$:

- for FS G08 (in the upper capsule)  
  $$T_F2 = 0.0008658(T_{G2})^2+0.05058(T_{G2})+310,$$
- for FS G41 (in the bottom capsule)  
  $$T_F1 = 0.0003044(T_{G1})^2+0.7774(T_{G1})+66.96.$$

The temperature for the bare kernel was taken to be the same as the measured graphite cup temperature ($T_K = T_{G1}$).

During irradiation release rates of major gaseous fission products (GFP) were measured by gamma spectrometry by means of sampling from an appropriate capsule into a Marinelli beaker (with a standard uncertainty of ±10%).

Temperature and Kr-88 R/B histories for the two irradiated FS are shown in Fig.10.

Measured R/B results for major GFP are shown in Fig.11 and Fig.12.
IV. DISCUSSION

1) Methodical reactor testing demonstrated:
   • the possibility of achieving target fuel central
temperatures stable within the required range of
   ±50°C using the Gas Handling System “RISK” (by
   means of controlled helium-neon mixtures) or by
   moving irradiation capsules along the core height.

2) GFP release from the upper capsule (with FS
   G08 only) originated almost entirely from U-235
   contamination in FS matrix graphite as the U-235
   mass in 185 g of FS matrix graphite, $(5.3±1.8)×10^{-7}
g$ U-235, is much greater than U-235 contamination
   of $4.9×10^{-9}$ g U-235 in oPyC layers of all 13 924
   coated particles in a FS.

3) GFP release from the bottom capsule (with FS
   G41 and a bare PBMR kernel) was dominated by
   GFP release from the bare kernel as the U-235 mass
   in the kernel, $(5.50±0.25)×10^{-5}$ g U-235, is much
   greater than that in the FS matrix graphite,
   $(5.3±1.8)×10^{-7}$ g U-235.

4) R/B curves of Kr-88 for both capsules were
   similar. Thus GFP release mechanisms for both
   capsules are similar.

5) GFP release values from FS are low in the
   temperature range between 1000 °C and 1100 °C,
   and fall in the range of $(5 to 10)×10^{-9}$ for krypton
   isotopes and of $(4 to 7)×10^{-9}$ for xenon isotopes and
   conform to modern requirements for initial U-235
   contamination of matrix graphite of HTR fuel
   elements.

6) Based on measured $R/B$ values, diffusion
   coefficients for major GFP in the fuel can be
   evaluated by the Booth formula [6]

   $$D_{Kr} = \frac{\lambda}{2} \left[ \frac{\lambda \cdot a^2}{D} \coth \left( \frac{\lambda \cdot a^2}{D} \right) - \frac{D}{\lambda \cdot a^2} \right]$$

   where $\lambda =$ decay constant (s$^{-1}$), $a =$ equivalent
   sphere radius (cm) [in our case $a = 252×10^{-4}$ cm];
   $R = 8.314$ J/(mol·K); $T_K =$ kernel temperature (K).

   Thus, the krypton diffusion coefficient (cm$^2$/s) in
   the PBMR UO$_2$-kernel at the temperature range of
   1070 to 1400 K can be expressed as:

   $$D_{Kr}^{UO_2}(T_K) = 3.37×10^{-10} \cdot \exp \left( - \frac{78 500}{R \cdot T_K} \right).$$

7) U-235 contamination in FS decreases from the
   outer PyC layer of coated particles to the FS fuel-
   free zone (Fig.7). It is evidence that release of U-235
   from outer PyC layers of coated particles into FS
   matrix graphite during manufacture of FS is the
   source of U-235 contamination of the FS matrix
   graphite. The evaluated ratio of total U-235 in the
   matrix to that in the fuel particles for the entire
   sphere is about $6×10^{-7}$.

V. CONCLUSION

The obtained results of pre-irradiation
characterization and methodical irradiation testing
were evidence of high quality of the PBMR pre-
production fuel spheres of lot FSA-J01.
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VII. REFERENCES


