BARC is the fountainhead of all research and development activities on nuclear fuels. At present major efforts are directed towards development of processes and technologies for $^{233}\text{U}$ based fuel for AHWR and Pu-based metallic fuels for future FBRs. In parallel, technology development is going on for fabrication of annular oxide pellets by using rotary press, establishment of welding parameters for D-9 tube and plug, automatic pellet inspection system, microwave dissolution and denitration system, keeping in mind requirement for the production of fuel for PFBR.
2. DEVELOPMENT OF FUEL FABRICATION PROCESSES AND TECHNOLOGIES

Apart from regular production of fuels for operation of research reactors, including FBTR, BARC is engaged in the development of ThO$_2$/U$_{233}$ based fuels for Advanced Heavy Water Reactor (AHWR) and Mixed Oxide fuels for Prototype Fast Breeder Reactor (PFBR). It is essential to introduce automation for this fuel fabrication. The fabrication of U$_{233}$ based fuel needs development of remotization in fuel fabrication inside shielded hot cells along with automation. Various activities in the development of fuel fabrication processes and technologies in connection with Th/U$_{233}$ based fuel & PFBR – MOX fuels are briefly highlighted in the following paragraphs.

2.1 DEVELOPMENT OF FUEL FOR AHWR

Several technologies for fabrication of (Th-U$_{233}$) MOX fuel are under development in the Nuclear Fuels Group at BARC. These include Sol-Gel Microsphere Pelletization (SGMP), Impregnation and Coated Pellet Agglomeration (CAP). The SGMP technique has already been demonstrated for fabrication of UO$_2$ fuel in technological scale. Impregnation technique and CAP techniques which are being actively developed at present are described below:

- **Impregnation Technique**

  Manufacturing of (Th, UO$_2$) pellets for AHWR by impregnation technique is being developed and the process has been demonstrated in Kilogram scale. This process has the advantage of requiring only a partially shielded facility as compared to completely shielded facility needed for the conventional powder metallurgy process being followed currently for ceramic nuclear fuel fabrication. It is also more amenable to automation and remotisation.

  The impregnation technique involves fabrication of low-density ThO$_2$ pellets having predominantly interconnected open pores, removal of entrapped gases from the pores by application of vacuum and impregnation of these pellets with 1.5M uranyl nitrate solution. Impregnated pellets are then dried and sintered at high temperature to achieve desired specifications. The molarity of the solution has been kept at this level not only for uranium content control in the pellets but also from criticality considerations. Apart from the molarity of the uranyl nitrate solution, the number of impregnation cycles and the time for impregnation are the factors controlling the uranium content and homogeneity of Uranium distribution in (Th, UO$_2$) pellets. An optimum impregnation cycle has been achieved to produce AHWR fuel pellets to specification.

- **CAP Technique**

  Process optimization studies are in an advanced stage of completion for CAP technique for fabrication of (Th-U$_{233}$) fuel pins for critical facility of AHWR using natural UO$_2$ to simulate U$_{233}$ oxide. This innovative technique has been successfully demonstrated for the trial fabrication of (Th-U)O$_2$ fuel pellets for AHWR critical facility.
In this process, ThO$_2$ powder is mixed with organic emulsion of required quantity and extruded through an extruder having perforated rolls. The extrudes are usually of 0.8 mm – 1.0 mm indiameter and 4 – 5 mm in length.

These extrudes are then loaded in spheroidiser where they are broken and rounded by a chequered plate rotating at an optimum speed. The ThO$_2$ spheroids are then coated with U$_3$O$_8$ material of desired percentage in an Universal Mixer. The coated spheroids obtained are then dried in an oven at 100°C for 1 hr and compacted in a Rotary press. The green pellets show network of U$_3$O$_8$ in ThO$_2$ matrix. The green pellets are then sintered in a furnace in an oxidizing atmosphere at 1450°C for 4-6 hours to obtain sintered pellets. The sintered pellets of desired specification show uniform distribution of UO$_2$ in ThO$_2$ matrix. The sintered pellets have successfully met the specifications of the fuel and various tests and analysis carried out on these pellets confirm the quality of the pellets.

This technique minimizes a number of operations and bulk material processing in unshielded facility. Handling of controlled quantity for efficient and faster fabrication is an added advantage. The material characteristics improve and offer greater flexibility to exert control on the higher yield of accepted quality pellets.

Fabrication of Th-Pu MOX fuel pins for the critical facility will be taken up shortly. A new glove box train for this purpose is being installed. Development work is also being carried out for making a prototype shielded facility for fabrication of fuel containing U$^{233}$.

### 2.2 TECHNOLOGY DEVELOPMENT

- **Annular Pellet Fabrication**

Technology for fabrication of annular pellets using indigenous rotary press has been developed. The necessary design of tooling for making annular pellets for both fast and thermal reactors has been made.

Using this design, MOX pellets containing oxides of natural uranium, U$^{233}$ and Pu required for making the 37 pin PFBR experimental sub assembly have been fabricated. The MOX
pellets in these fuel pins are of a diameter of 5.56 mm with a central hole of dimension of 1.6 mm. The fuel assembly is undergoing irradiation in FBTR.

MOX fuel pellets (containing 44% PuO₂) for making MOX fuel pins for the hybrid core of FBTR are being made using this technology. Additional fabrication lines are being installed using advanced process equipment like Attritor, Rotary Press and Sintering Furnace. The fabrication equipment installed is all indigenously developed. A number of automation systems for use in fuel pelletisation line and fuel pin welding line have been developed. The systems are being installed in the new fabrication lines.

- **Microwave heating System**

A three KW micro wave heating system has been designed and installed at AFFF based on the experience of the operation of a 700 W stainless steel microwave oven made earlier. Necessary modifications were made to make the system glove box adaptable.

The three KW microwave oven has been commissioned for use inside the glove box. The flow sheets for dry and wet recycling of MOX fuel scrap have been developed. Experimental MOX fuel bundle using micro wave processed feed material has been loaded in PHWRs.

- **Welding Technique for D9 Tube & Plug**

The fuel pins for PFBR use advanced D 9 material for cladding tube. Annular MOX pellets are encapsulated in the thin walled D 9 tubes by TIG welding of end plugs at both the ends. Technology has been developed for welding of the end plugs with the D 9 clad tubes. The fuel pins both for the experimental sub assembly and for the hybrid core for FBTR have been made using this technology. The same technology will be used for welding of three meter long PFBR MOX fuel pins.
Ultrasonic Testing Technique of PFBR Fuel Pin End Plug Welds

The end plug welds for the Fast reactors are currently being evaluated by X-radiography. An ultrasonic immersion technique has been developed for evaluation of these end plug welds.

Automatic Pellet Inspection System

Sintered Uranium / Plutonium / Thorium-based oxide / carbide pellets are used as fuel for thermal and fast reactors. These pellets are radioactive & radiotoxic and give rise to personnel exposure on handling. The stringent specification on variation in diameter, linear mass etc. and very low tolerance of surface defects, make 100% physical inspection of these pellets mandatory and a highly challenging task. A new version of automatic pellet inspection system consisting of automatic vision system and laser metrology system is being developed for convenient, accurate and fast inspection of these pellets. This unit can be used for inspection of sintered pellets needed by all types of nuclear reactors. The schematic layout of the inspection system is shown below.

Video Microscope Imaging System

Microstructural evaluation of MOX pellets and end plug welds is presently being carried out using special glove box model microscope which has the objective and related optical components inside the glove box. A video microscope imaging system using CCD camera has been developed for glove box use. It consists of CCD camera, monitor, frame grabber and printer. The entire optics is kept outside. The sample is mounted vertically on a special stage inside the glove box but near the glass of the glove box. The system is being used for routine quality control of MOX pellets and active end plug welds at BARC facilities at Tarapur.
A five axis weld scanning set up has been developed for positioning the probe precisely and indexing the tube. Angle beam technique has been used for the testing. Experiments have been carried out with standard defects and a large number of experimental welds. Good correlation has been obtained with X radiography and metallography.

2.3 DEVELOPMENT OF METALLIC FUEL FOR FAST REACTOR

Physical Metallurgy of Uranium Alloys

U-Zr is a candidate metallic fuel for fast research-reactor. However, U-Pu-Zr can be used in power reactor. In order to develop the U-Pu-Zr fuel, the first judicial step would be to get accustomed with U-Zr system. These alloys are produced by vacuum induction or arc melting technique. Solubility of various alloying elements is different in different phases. α phase can not dissolve any element beyond 0.3%; the extent of dissolution varies from element to element and also with temperature. β phase can dissolve alloying elements to the tune of 1%. Alloying elements, like Mo, Nb, Ti, Zr can form a solid solution with γ phase with a concentration varying from 20% to 100%, while Au, Pd, Pt, Re, Rh, Ru and V are soluble to γ phase in the range of 2% to 10% concentration. In U-Zr system, for example, γ-U can dissolve 100 a/o Zr but β phase can dissolve a maximum of 1 a/o Zr at 965 K and alpha phase can dissolve only about 0.6 a/o Zr max. at 935 K. By and large slow cooling permits the γ phase to decompose to two-phase structures morphologically similar to pearlite in steel. Rapid quenching suppresses these diffusional decomposition modes, resulting in various metastable phases. Moreover, quenched structure is quite sensitive to gammaizing temperature and cooling rate, implying that stresses due to quenching, ordering and/or retained vacancy concentrations are important.

RE-EVALUATION OF U-ZR PHASE DIAGRAM:

The following notation is used for the free energy of mixing; in \( \Delta G^a_{\alpha,\gamma}(\delta,\gamma) \), superscript indicates the phase of concern; first term inside the parenthesis indicates the standard state of component A and the second one indicates the same for component B.

Unfortunately, thermodynamics can not predict the formation of probable phases for a given system. In order to identify the phases, for a given system, there are two available options; either by standard experimental technique (e.g. specific heat capacity measurement, high temperature XRD etc.) or by first principle electronic calculations.

U-Zr system manifests the following phases, excluding the phases of pure components – Liquid (completely miscible), γ(solidsolution of γ U and β Zr, bcc), γ’ and γ” (formed due to spinodal decomposition of parent γ phase), β-U (U-rich solid solution, tetragonal), α-U (U-rich solid solution, orthorhombic), α-Zr (Zr-rich solid solution, hcp) and δ (non-stoichiometric intermetallics compound, primitive hexagonal).

The next task is to find the equations for the free energy of mixing. It is of utmost importance that while applying the common tangent construction it must be ensured that for all the phases the designated standard states should be same for individual components. For the present case α-U and α-Zr are chosen as the standard state for U and Zr respectively. Forming the equation of free energy of mixing will be elaborated below only for the liquid phase.

\[
\Delta G^a_{\alpha}(L,L) = \Delta G^a_{\alpha}(L,L) + \Delta G^a_{\gamma}(L,L)
\]

The last two terms on the right hand side of the above equation are the changes in free energy when pure U (and pure Zr) melts from its α phase. Basically, \( \Delta G^a_{\alpha} \) and \( \Delta G^a_{\gamma} \) are.

\[
\Delta G^a_{\alpha}(L,L) = \Delta G^a_{\gamma}(L,L) + \Delta G^a_{\delta}(L,L)
\]

and

\[
\Delta G^a_{\gamma}(L,L) = \Delta G^a_{\delta}(L,L) + \Delta G^a_{\gamma}(L,L)
\]
Clearly, such equations can be written for all the phases:

\[
\Delta G^{\text{U-\text{U}}} (a, a) = \Delta G^{\text{U}} (L, L) + X^\text{U} \Delta G^{\text{U}} (a) + X^\text{U} \Delta G^{\text{U}} (\text{a})
\]

\[
\Delta G^{\text{U-Zr}} (a, a) = \Delta G^{\text{U}} (\gamma, \beta) + X^\text{U} \Delta G^{\text{U}} (a) + X^\text{U} \Delta G^{\text{U}} (\gamma)
\]

\[
\Delta G^{\text{Zr-Zr}} (a, a) = \Delta G^{\text{Zr}} (\text{a}) + X^\text{Zr} \Delta G^{\text{Zr}} (\gamma)
\]

\[
\Delta G^{\text{Zr}} (a, a) = \Delta G^{\text{Zr}} (L, L) + X^\text{Zr} \Delta G^{\text{Zr}} (a) + X^\text{Zr} \Delta G^{\text{Zr}} (\text{a})
\]

\[
\Delta G^{\text{Zr}} (\gamma, \beta) + X^\text{Zr} \Delta G^{\text{Zr}} (\gamma) + X^\text{Zr} \Delta G^{\text{Zr}} (\beta)
\]

\[
\Delta G^{\text{Zr}} (\beta, \gamma) + X^\text{Zr} \Delta G^{\text{Zr}} (\beta) + X^\text{Zr} \Delta G^{\text{Zr}} (\gamma)
\]

\[
\Delta G^{\text{Zr}} (\gamma, \beta) + X^\text{Zr} \Delta G^{\text{Zr}} (\gamma) + X^\text{Zr} \Delta G^{\text{Zr}} (\beta)
\]

\[
\Delta G^{\text{Zr}} (\beta, \gamma) + X^\text{Zr} \Delta G^{\text{Zr}} (\beta) + X^\text{Zr} \Delta G^{\text{Zr}} (\gamma)
\]

The apparent deviation of the transition temperatures for U are attributed due to the presence of Al in U to the tune of 0.1 wt% which was confirmed by the chemical analysis and supported by the Al-U phase diagram.

**Metallographic Techniques:**

Pure uranium as well as most of the uranium alloys are highly prone to oxidation. It is not uncommon to observe that metallographically polished sample get tarnished within one to two hours of exposure in air. Moreover polygonization takes place very easily both in pure uranium and in dilute uranium alloys resulting in irregular and massive grain structure; unlike the classical equiaxed grains. Hence apparently there are no high energy regions to respond in chemical etching.

The inclusions present in the alloys can readily be seen in polished sample with conventional bright field mode as well as in SEM. The major inclusions present in uranium and its alloys are oxide, carboxinitride, hydride, nitride and carbonitride. The morphology of the inclusions and their chemical nature (i.e. oxide or nitride or hydride etc.) are established and well documented.

For alloys with higher concentration of alloying element, chemical etching can be employed. For U-Zr alloys, there are several chemical etchants listed in literature. A series of microstructures are presented here that are self explanatory.
Injection Casting Process For Metallic Fuel Pins

It is planned to use metallic fuel for FBR/PFBR reactors due to its short doubling time. Keeping this in view work was initiated in Nuclear Fuels Group, BARC in mid 2004 for development of injection casting process for production of pure uranium and U-Zr alloys rods of 6 mm dia. Injection casting process was chosen due to the following advantages.

- the process is simple and fast
- possibility of multi-mould casting.
- capability of producing precision castings with higher L/D ratio.
- the process can be applied to variety of alloy compositions and
- amenable to remote operation.

In this process, a bunch of one-end closed precision-bore quartz moulds are suspended with open end down, with the help of a suitable fixture above the graphite melting crucible. The furnace is evacuated to the required level of vacuum and the metal is melted and heated to a pre-determined superheat using induction power source. The moulds are lowered to the required depth in the molten metal and the chamber is isolated. The furnace chamber is then pressurized with argon gas to a set pressure for forcing the molten metal in the evacuated moulds. After the castings are solidified, the moulds are raised and removed from the fixture and subsequently, the castings are removed by breaking the quartz moulds.

A suitable set up consisting of graphite crucible integrated with quartz tube moulds was fabricated and installed in the existing vacuum induction melting and casting furnace for experimental purposes. Uranium and uranium zirconium alloy rods of 6 mm dia. and 10 mm dia. and length ranging between 300-350 mm were successfully produced and evaluated.
Procurement of an injection casting set up suitable for being installed in the glove box is in process. After carrying out initial trials with U-Zr alloys, the system will be installed for fabrication of Pu-U-Zr alloy fuel pins.