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## Chapter 4

## From Ore to Core – Competence In Materials Technology



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### **Captions for Photo-Collage**

1. *Seamless zircaloy calandria tubes fabricated at NFC, Hyderabad for PHWR reactors.*
2. *Beryllium scan mirror fabricated at Beryllium pilot plant, Mumbai.*
3. *Zirconium crystal produced at BARC, Trombay*
4. *Dr Brahm Prakash and Dr Bhabha with Prime Minister Lal Bahadur Shastri at AEET ( Presently BARC), Trombay .*
5. *Post Irradiation dimensional measurement of pressurized capsule*

## Materials Requirements of DAE and Their Development

The nuclear industry has rather unique materials requirements not prevalent in any other industry. These requirements stem from considerations pertaining to the neutron cross section for specific processes like fission, absorption and scattering and to the aggressive conditions encountered in various operations. Further, safety, reliability and efficiency of nuclear reactors and other installations, place stringent demands on the performance and integrity of the materials used in the manufacture of various components and systems. In nuclear reactors, the presence of intense radiation in addition to thermal, mechanical and chemically aggressive conditions, result in challenging requirements that severely constrain the choice of materials. For example all structural materials used inside a thermal reactor core should have very small neutron capture cross section apart from the other usual requirements. But, control rods on the other hand should have large absorption cross-section for neutrons. The core components including the clad and wrapper materials, made of zircaloy in PHWR and austenitic stainless steels in FBR, are subjected to significant radiation damage. Hence, the materials used for these components should have good radiation resistance. The coolant and calandria tubes, main vessel, inner vessel, intermediate heat exchangers (IHX), core and grid support plates, and most other structural materials must also be so selected and processed as to perform satisfactorily over the entire lifetime of the reactor. Steam generator materials are mainly constituted of chromium-molybdenum containing ferritic steels having good high temperature resistant properties. The nuclear fuels used in most commercial reactors are ceramics suitably clad and wrapped as fuel elements. The structural integrity of these nuclear fuel elements constitutes the first level of defense against the leakage of radioactivity to environment. Additionally control rod and structural materials, coolants etc are sources of special requirements. Indeed each reactor type uses a combination of different metals, alloys and ceramics specifically suited to its design. Since these materials requirements are unique to the nuclear industry, the Departments of Atomic Energy has had to pioneer activities starting from the production of special materials to the eventual manufacture of a large variety of finished components.

Indeed, the entire gamut of activities, beginning with extractive metallurgy and purification of nuclear materials from their ore, alloy design and melting, characterisation, testing and component fabrication, assessment of irradiation behaviour and the development of advanced materials and processes etc, constitute the wide spectrum of fascinating activities in metallurgy and materials science undertaken by DAE. This chapter discusses various aspects of materials development like processing of minerals, extractive metallurgy of rare metals, powder metallurgy of Be, fabrication of fuel elements and control rods for reactors, development of ceramics like  $\text{UO}_2$ , fabrication of cold rolled joints for pressure tubes, development of welding technology, plasma nitriding, work on sodium moderator for fast reactors and production of heavy water. All these activities have led to a comprehensive mastery of all materials processing, development and component manufacture methodologies required for nuclear reactors and related technology.

The development of Wootz steel and the rustless wonder - the Iron Pillar at Delhi, are testimony to the rich heritage of material and metallurgical science in India. The indigenous development of advanced alloys and processes to support the nuclear programme is but a continuation of the glorious tradition of excellence in this discipline.

### Sands to Wealth - IREL History

Since the science of materials starts with the production of the basic raw materials, it would be appropriate for us to start here. The initial discovery of the rare mineral deposit in India on the western coast has a quaint history: In the year 1909 a German chemist named Schönberg observed the presence of the mineral monazite, a radioactive mineral containing thorium, in the coir (a coconut fibre), shipped to Germany from India. He traced it back to the place from where the coir was exported and this led to the discovery of the placer deposits of these minerals on the western coast of India, in the erstwhile princely state of Travancore

The beach sand industry itself has a history of about a century and as early as 1911 it found the beach sands to be a rich source of raw materials. Even at that time, it began to convert beach sands to wealth by exporting rare earths



*Beach sand mineral deposit along the coastal belt of Kerala*

produced from the sands. It also began supplying useful rare materials like zircon, thorium and rutile to nuclear, chemical and metallurgical industries. This thriving industry which started in Manavalakurichi (MK) (presently in Tamilnadu state) and subsequently in Chavara (presently in Kerala state) was exporting monazite and ilmenite (a titanium based mineral present in the beach sand).

This activity continued unabated till 1947 and came to near closure in the late 50's, when Govt. of India realized the strategic importance of the minerals and placed an embargo on its export. In view of the growing demand for rutile and zircon, the Government of India wanted to restart beach sand industries operated by private entities and entrusted the industry to IREL in 1965. With this, the beach sand industry in India entered a period of transition and the subsequent years witnessed changes in mining operations, mineral processing, mineral beneficiation and value additions through active research & development programmes. IREL has been operating a rare earths processing plant at Udyogmandal, Cochin since early 50's. IREL also set up a thorium processing plant at Trombay in the mid 50's and took over MK and Chavara mineral processing establishments in the the mid 60's. Subsequently, in the mid 80's an integrated industrial complex known as Orissa Sands Complex (OSCOM) was built near Chatrapur town in Orissa state consisting of mining, mineral processing and synthetic rutile (a value addition to ilmenite mineral) manufacturing plant.

### **Growth of Mineral Production Activities**

IREL started several programmes to modernize the old plants at MK and Chavara with technology input. A zircon-rutile plant was established at MK to exploit stockpiled ilmenite tailings for

the production of rutile and zircon. A flow sheet was developed for the production of 4,000 tons per year (tpy) of monazite required as feedstock to Rare Earths Division (RED), Alwaye for production of rare earths which have high export potential. In 1972, a major decision was taken to change the process flow sheet wherein high-tension separation was envisaged as the initial operation in place of the older technology of magnetic separation. This helped in increasing the throughput capacity with the addition of a few equipments. Subsequently, in 1978, a pre-concentration plant was commissioned to upgrade depleted raw sands and also to expand the resource-base by mining the dune deposits adjacent to the plant area. The inception of this plant and integration with mechanized mining gave a new lease of life to the operating plants as low-grade sand could now be beneficiated to over 90% heavy minerals (HM).

The Chavara plant was commissioned in early 1971 after having been taken over from private entities. Refurbishment was done and the capacity of the plant was enhanced to cater to the increased demand of ilmenite. An integrated system of dredge and wet concentrator was developed with suitable process changes to use low grade sand. The first plant known as Mineral Recovery Plant was commissioned in 1990 and the second plant was commissioned in 1996. A zircon opacifier plant was established to process zircon into zircon flour and micron sized zircon as value added products in the late 70's and subsequently the wet grinding and classification facilities were added.

To exploit the natural beach sand resources in the east coast of the country, IREL initiated the setting-up of an integrated industrial complex known as Orissa Sands Complex (OSCOM) near Matikhalo village, south of Chatrapur town in Orissa. IREL started developing the deposit from 1975 and commissioned the mining and mineral separation facility along with a chemical plant for the production of synthetic rutile from Ilmenite in the year 1986. The deposit is one of the largest virgin beach sand mineral resources in the world consisting of 240 million tons of raw sand containing 18-20% heavy minerals. The mining was planned to be carried out at a rate of 500 tons per hour (tph) using a dredge coupled with a pre-concentration system. The mineral processing plant was designed to produce 2.2 lakh tonnes of ilmenite and associated minerals such as rutile, zircon, monazite, garnet and sillimanite etc. A Synthetic Rutile



## *Tracking the past of self reliant nuclear technology*

The growth of atomic energy in India is the story of a total technology development. When we embarked upon the ambitious nuclear programme, the technology infrastructure in the country was in an infant stage. It was, therefore, necessary to start practically every activity from the scratch. Let me explain this point with a few examples.

The first and foremost requirement of the development of any specific industry is to have the access to the right materials. Therefore, in our indigenous nuclear programme an emphasis was placed right from the beginning in building the capability of processing and production of nuclear materials – all starting from indigenous resources. Geological prospecting of atomic minerals, mining and mineral processing, metal extraction and processing of uranium, thorium, zirconium, their alloys and important compounds and their fabrication into in-core reactor components were given the necessary thrust in the early stage. Parallely, efforts for production of heavy water were initiated. All these activities, necessarily demanded laboratory scale process development, optimization of process parameters in pilot scale and setting up of full scale production facilities. Recognising the fact that in our country the reserve of uranium minerals is modest and that of thorium is very large, we have committed to the three-stage programme which provides the added advantage of substantial reduction of the radioactive waste burden. Technology development with respect to the spent fuel reprocessing and to the radioactive waste management has also been given the due importance from the early stage of our programme. Behind today's success of the nuclear energy programme lies our core competence in processing and production of all the necessary nuclear materials.

The path of development on such a wide front has not been free of obstacles. While scientists working in the laboratory examining alternate processing methods had serious constraints in getting access to characterization tools, their engineering partners responsible for translating the laboratory work into plant scale operation had to depend entirely on indigenously built plant equipment. The technology denial

regime forced the scientists and engineers to catalyze the development of basic equipment and facilities within the country. For example, vacuum pumps and equipment, several electron and laser beam processing systems, high speed rotating machines and remote handling machines have all been developed in-house. Technology transfer which followed yielded a multiplier effect for production of many such systems by Indian industry. Today, we are reaping the benefits of this difficult and tortuous path of indigenous development as we take up building of systems associated with further technological complexities, namely, synchrotron machine, advanced nuclear reactors and accelerator based systems.

The next example to be cited is that of computers. One of the first digital computers (TDC-12) in the country was built in Trombay. The development of parallel computers with steadily increasing speeds has always maintained the pace with the increasing demands of computational capabilities from the scientific and engineering community.

Having operated nuclear reactors for over four decades, necessary technologies have been developed for the assessment of health of different critical reactor components, quantitative evaluation of their residual lives and repair or replacement of these as necessary.

The present volume narrates the exciting story of the all-round technology development as it happened in the atomic energy programme – which has taken the country in the league of technologically developed nations. As scientists working in this Department, we are fortunate to have the ring side view of this exciting and challenging development.

**S. Banerjee**

Director,

Bhabha Atomic Research Centre

Plant (SRP) was set up with acid regeneration system to produce 1 lakh ton of synthetic rutile, a value added product of ilmenite.

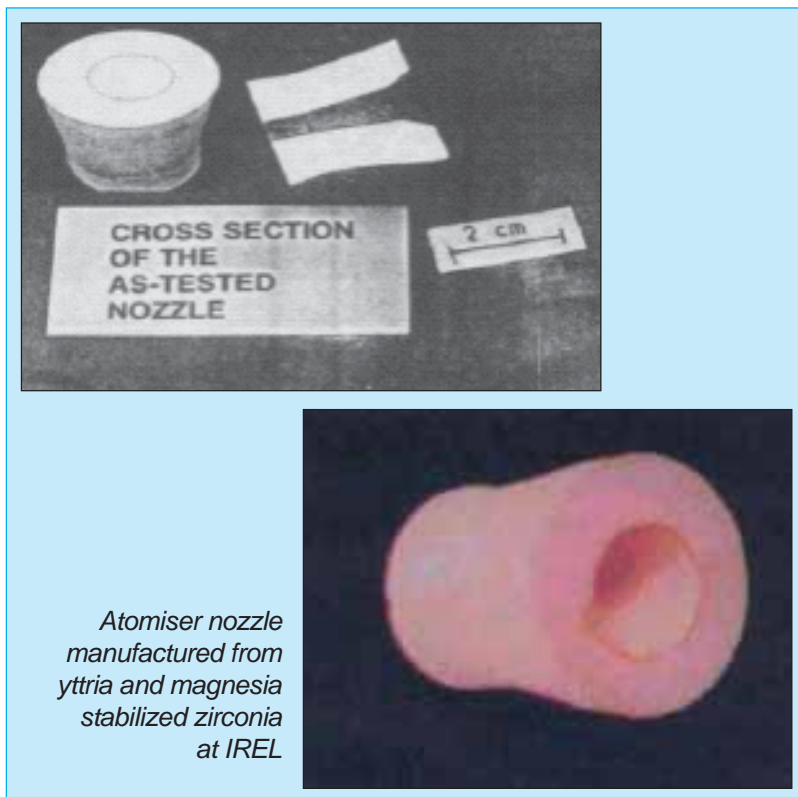
During these years IREL modernized its plants continuously in line with the development in the beach sand mineral industry elsewhere in the world. In this process IREL assimilated considerable extent of foreign technology and contributed significantly towards the fulfilment of the broad based objectives of the Govt. of India.

### Research & Development Activities of IREL and its Diversification

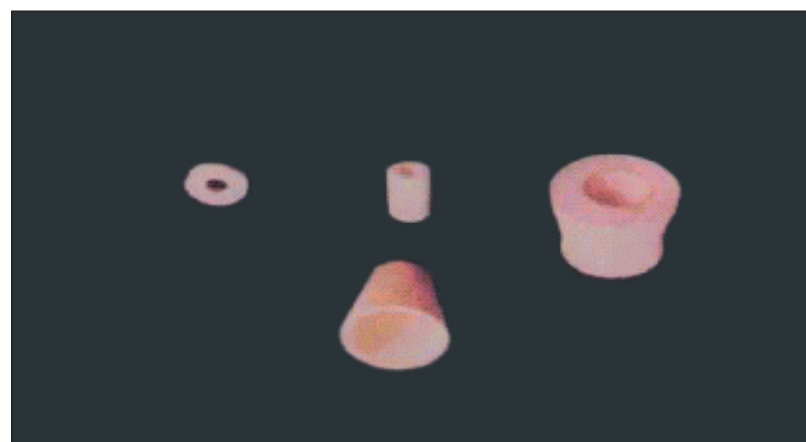
There are three dedicated laboratories, which cater to the various needs of IREL. The first is located at Kollam, Kerala (Indian Rare Earths Research Centre (IRERC)), the second is at OSCOM, Chatrapur and the third is at RED, Alwaye.

The developments related to zirconia, yttria and magnesia are of industrial interest. The good high temperature properties of zirconia are attractive for the development of components for adiabatic diesel engines, extrusion dies, cutting tools, grinding media, pump wear parts, seals, insulations, ceramic filters and coatings. In fact, high purity zirconia is also used for making oxygen sensors, piezoelectric and electro-optical devices and capacitors. American diamond (an artificial gem) is produced from the molten solution of zirconia in presence of yttria. Various coloured stones can also be produced by adding rare earth oxides to it.

Some of the significant Research and Development activities pertaining to these materials are elaborated. In the laboratory, the co-precipitation technique was developed to produce fully stabilized as well as partially stabilized zirconia for structural ceramic applications by doping it with calcia, magnesia and yttria in the initial phase of R&D programme. Later, attention was given to the development of process for producing ceria stabilized zirconia in cubic and tetragonal crystal forms as cerium is one of the dominant rare earth elements present in monazite recovered from beach sand deposits. The structural ceramic components made out of ceria stabilized zirconia produced in the laboratory had shown very high fracture toughness in the range of 16 to 25 MPa m<sup>1/2</sup> and the sintered component consisted of 95 to 100% tetragonal phase. The laboratory in collaboration with Central Glass and Ceramic Research



*Atomiser nozzle manufactured from yttria and magnesia stabilized zirconia at IREL*



*Ceramic components manufactured using yttria and magnesia stabilized zirconia nozzles at IREL*

Institute (CGCRI), Kolkata, Defence Metallurgical Research Laboratory (DMRL), Hyderabad and Department of Science & Technology, New Delhi worked out a project for developing technology for producing critical components for application in iron and steel industries. Also, a few atomizer nozzles were fabricated from the magnesia and yttria stabilized zirconia produced in the laboratory for use in super alloy melting. The fabrication of the nozzles was carried out at CGCRI, Kolkata and field trials were conducted at DMRL, Hyderabad. The tests have confirmed suitability of zirconia powder for producing components with dense microstructure without sacrificing thermal shock

resistance. The internal bore of the nozzles was found intact when molten super alloy at 1883 K was poured through the nozzles.

A process was developed for producing high purity zirconia containing very low impurities of iron oxide (<10 ppm), silica (<100 ppm) and titania (<30 ppm). The zirconia produced in the laboratory was tested successfully for commercial production of single crystal cubic zirconia artificial diamond gem. A pilot plant was designed and constructed with the above know-how to produce 3 to 3.5 tonnes per annum of various grades of zirconia and zirconium compounds. The construction of the pilot plant was based totally on in-house capability, including the development of process flow sheet, engineering flow diagram, selection of equipment and materials of construction, fabrication and erection of equipment and pipeline etc. The plant was commissioned in the year 2000. In the plant the waste silica generated during frit dissolution was also converted to useful products. Some of the zirconium based products produced in the pilot plant are high pure gem grade zirconia; magnesia, ceria, yttria stabilized zirconia in tetragonal and cubic crystal structures; calcia stabilized zirconia in cubic crystal structure; zirconium carbonate; hydrated zirconia; zirconium basic sulphate etc. Process development work is presently under progress to produce nano scale particle stabilized zirconia.

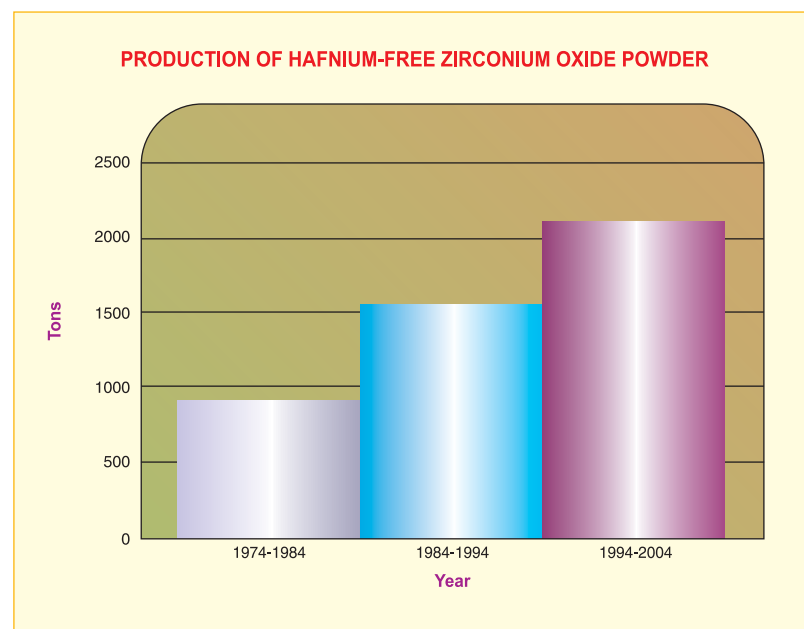
### Nuclear Grade Zirconium Oxide

Zirconium based alloys are selected as clad, wrapper and pressure tube materials in PHWR's mainly for neutron economy. Preparation of nuclear grade zirconium oxide constitutes an essential intermediate step in the production of zirconium metal from the ore, viz. zircon, which is a silicate containing about 65% zirconium oxide, 1.5-2.5% hafnium oxide and small amounts of other metal oxides like  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  etc. Since most of the impurities present in zirconium oxide are retained during its conversion to metal, the purity desired for the metal has to be ensured at the oxide stage itself. Also, Hf which is a commonly co-occurring element with Zirconium ore, is a neutron poison with high absorption cross-section. The presence of Hf in zircaloy can jeopardize sustainability of the chain reaction in the reactor. Hence, intensive research was directed to ensure development of process sequence to bring down the natural level of about 2.5% hafnia in zircon to less than

100 ppm hafnium in zirconium. Research in halide metallurgy commenced in the fifties and was directed towards separation of hafnium from zirconium.

Based on laboratory scale studies and semi-pilot plant trials, a process was developed for preparation of hafnium-free zirconium oxide starting from zircon sand. The design of a plant for producing 125 tonnes/year of zirconium oxide was then carried out and the plant was set up at Hyderabad as a part of the Nuclear Fuel Complex. This plant started production in 1971 and was the first plant to be commissioned at NFC. The process of obtaining nuclear grade zirconium oxide from zircon involves three main steps:

1. Treatment of the ore to bring the zirconium and hafnium values in soluble form.
2. Separation of zirconium from hafnium and other impurities.
3. Conversion of the purified zirconium solution to zirconium oxide.



*First batch of Hf-free zirconium oxide powder was manufactured in April 1971*

For the crucial separation of hafnium from zirconium in nitric acid medium, solvent extraction technique has been employed using tri-butyl phosphate solvent. In this process, the reaction mass of caustic fusion of zircon, containing sodium silicate and sodium zirconate, on leaching with water yields zirconium hydroxide leaving sodium silicate in solution. Filtration, drying

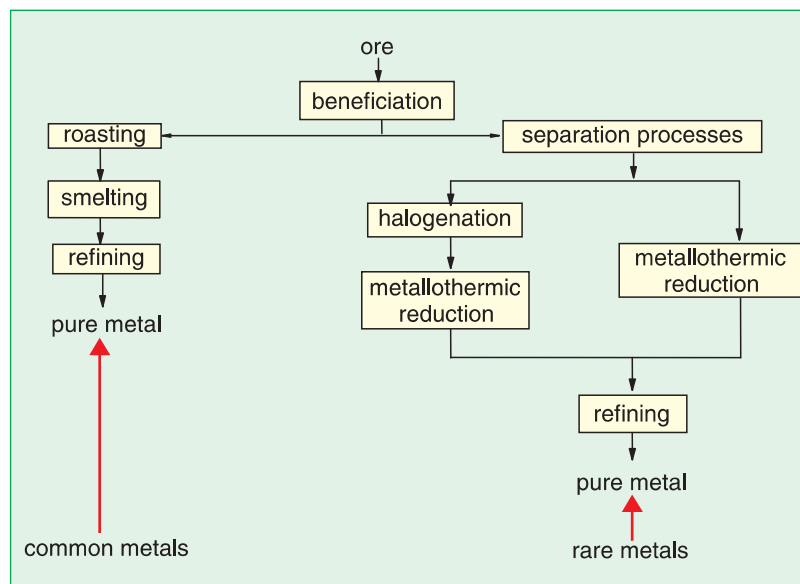
(dehydration) and dissolution in nitric acid give a crude solution of zirconyl nitrate. The separation of zirconium and hafnium from this solution is effected by selective extraction of zirconium in 50% tributyl phosphate. Pure zirconium solution obtained on scrubbing and stripping of the extract is converted to oxide by precipitation of hydroxide and its calcination.

During the development of pure zirconium oxide for nuclear applications in sixties, it was found that there is also a good demand for zirconium compounds in various other industries. Zirconium oxide finds use in ceramic stains for colored glazed tiles, high temperature refractory materials and in glass polishing. It is also used in alkali resistant glasses and as opacifier. On the other hand, zirconium oxychloride finds application in leather processing, textile processing, cosmetics etc., and is an important intermediate in the preparation of zirconium compound.

The process developed by DAE for producing chemically pure zirconium oxide and oxychloride was used as a spin-off technology and was taken up for production to cater to the domestic demand. Subsequently this technology has also been transferred to private industries. In this process, for non-nuclear industrial applications, separation of zirconium and hafnium is not attempted. The aim is to get the zirconium compound along with associated hafnium, purified with respect to other impurities present, such as silica, iron titanium, aluminum etc. Zirconium oxide is produced starting from crude oxychloride solution. The purifying step is precipitation of a basic sulphate of zirconium at controlled acidity and temperature. Conversion to hydroxide and calcination gives pure zirconium oxide as a fine powder, with purity better than 99.5%

### Nursery of Rare Metal Extraction

The beginning of atomic energy programme in our country witnessed the emergence and growth of several new technologies that were either totally unconventional or were less common areas of industrial practice. An important example is the development of extractive metallurgy for obtaining the less common metals particularly required for service in the nuclear reactor core and similar systems. The metallurgy programme thus focused, inter alia, on the development of suitable processes that could be used for production of pure zirconium, niobium, tantalum, titanium, hafnium, beryllium and selected



materials based on these metals, as well as the element boron and its compounds.

Extractive metallurgy consists of the science and art of winning metals commercially from the mined ore. For most of the common metals, extractive metallurgy means the routine sequence of roasting, smelting and refining operations. However, this scheme failed to work in the extraction of many of the rare metals. Rare metals occur in nature mostly in very low concentrations and in complex forms. Recovering metal values from these ores therefore involves very elaborate and complex processes requiring special equipment and skill. Further, these metals show a high degree of sensitivity to specific impurities, which influence pronouncedly their physical, chemical and metallurgical properties. This dictates that the rare metals be properly protected at every stage of their production and use.

Elaborate flow sheets were developed for various metals independently comprising of the process steps beginning from the pure compound intermediate, reduction and refining steps ending, in some appropriate cases, with the operations of ultra-purification. The production of ultra high purity metals is a challenging task. The challenge has been successfully met leading to the build up of a huge and effective knowledge base with adequate experience and facilities that has fondly been referred to as the nursery for reactive and refractory metals production techniques in India.

Halogens and halide chemistry have an important role to play in almost all stages of rare metal extraction, beginning from ore beneficiation to metal purification. The major technological



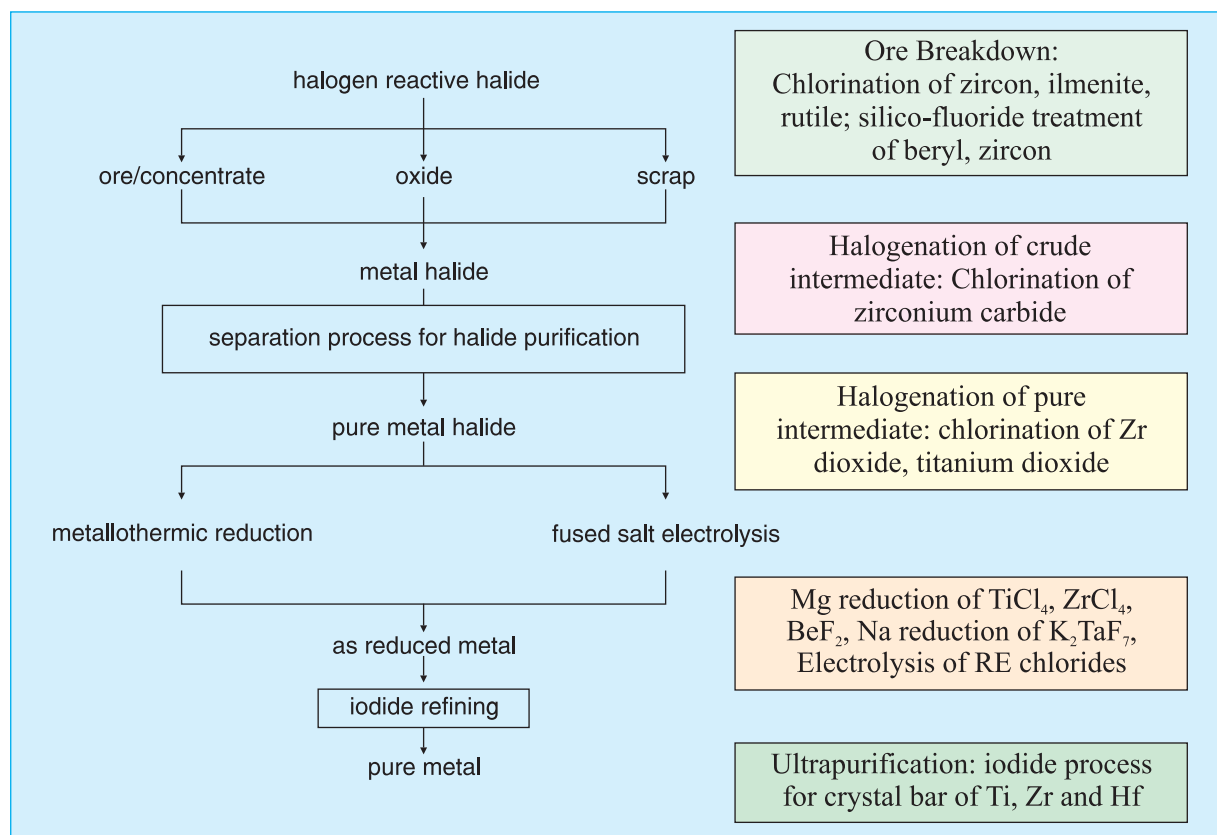
problems with use of halides and their vapors is their corrosive and reactive nature. This restricts the choice of the material of construction and the type of equipment for any large-scale operation. Nickel is compatible with fluorine and fluoride vapors upto 1073 K. Nickel and inconel alloys can withstand chlorine only up to 873 K. Hence, in the production of  $ZrCl_4$  or  $TiCl_4$  that involve temperatures of 973 – 1173 K, one has to use quartz or silica in the reaction zone. Further, a halogenation plant would also include provision for safe metering of the corrosive halogens and the safe disposal of the unreacted halogens by neutralizing with alkali or otherwise, due to their high toxicity.

Both pyrochemical as well as hydrometallurgical separation processes were tried out in the early years. It is technological history now that the commercially acceptable separation process happened to be a hydrometallurgical operation based on solvent extraction. That this solvent extraction process is still not fully acceptable is suggested by periodical revisits to the separation problem by research groups all over the world. The problem was revisited in the late 1980s and the 1990s and a pyrochemical process was then developed for effecting the separation. A usable difference in the volatility of  $ZrCl_4$  and  $HfCl_4$  was arrived at when the chloride mixture was evaporated from

a  $KCl-AlCl_3$  salt melt. The  $HfCl_4$  becomes more volatile leading to preferential retention of  $ZrCl_4$  by the melt. The process developed and tested successfully in a 100 mm sieve plate extractive distillation column, was eventually handed over to the NFC for utilization on a plant scale.

Synthesis of rare earths in metallic form is normally carried out by either metallothermic reduction of halides or oxides, carbothermic reduction or electrolytic reduction. The metallothermic reduction of halides involves using metals like sodium, magnesium or calcium as the reducing agent. Depending on the physical properties of the reactants and products and the heat of reaction, the product metal is recovered as an ingot, sponge (Zr, Ti) or powder (Ta). The reduction processes developed for Zr, Ti, Ta and Be serve as fine examples of process metallurgy of fluorides and chlorides realized on an industrial scale for the production purposes. The exothermic metal reduction processes fall under two major categories – (i) adiabatic (thermit type) and (ii) isothermal (Kroll type). The Kroll process which was nurtured and developed extensively, is exemplified by the magnesium reduction of zirconium tetrachloride. This process was tested on pilot plant scale, eventually producing 15kgs of sponge per batch with excellent reproducibility, before the process technology was transferred for regular large scale production. Similar reduction and pyro-vacuum distillation equipment have been tested and found to be suitable for production of titanium, thorium and hafnium metals as well. Based on the parallel investigation on titanium sponge production and pilot plant demonstration, a larger production plant for the production of titanium was set up at Defence Metallurgical Research Laboratory in Hyderabad.

For the production of tantalum powder from  $K_2TaF_7$ , a liquid-liquid reaction technique was developed. Filtered high purity



liquid sodium is continuously metered under argon cover on to the stirred mass of molten  $K_2TaF_7$  and NaCl kept at 1073 – 1173 K in an inconel 600 reactor. Tantalum metal powder is recovered from the reduced mass after leaching out the by-product fluorides with a sequence of aqueous reagents. This know-how was used to set up a production plant at NFC to produce up to 1 ton of capacitor grade tantalum per annum.

Beryllium metal is produced in the form of pebbles by the magnesium reduction of  $BeF_2$  in a graphite crucible heated in an induction furnace at 1373 – 1673 K. The metal pebbles, owing to their lightness, float to the surface of the slag. This process is now used on a pilot plant scale for production of the metal and its alloys to meet indigenous requirement.

Pioneering work has also been done in the area of metallothermic reduction of oxides. As specific examples of the advances, reference may be made of fairly large-scale production processes operated for preparation of zirconium, hafnium and thorium metal powders through calciothermic reduction of their respective oxides. Another notable advance has been in the aluminothermic reduction technology applied with great ingenuity in the preparation of niobium, tantalum, vanadium and molybdenum.

A metallothermic reduction process that does not generate excess heat and thereby avoids growth or sintering of reduced metal particles is highly conducive to metal powder preparation. Calcium reduction of zirconium dioxide at 1173 K generates only around 43 kcals per g mole of oxide. Further, when the reduction is carried out in the presence of a heat sink like  $CaCl_2$ , very fine metal powder (predominantly 3 micron size) results, dispersed in a matrix of CaO and  $CaCl_2$ . The metal powder is recovered from the reduced mass by careful aqueous leaching and drying. This technique has led to the establishment of a production facility of zirconium powder at NFC. Calciothermic reduction has also been investigated in detail for the preparation of hafnium, thorium, niobium and tantalum metal powders from their oxides. The process essentially consists of mixing the charge of calcium metal granules, metal oxide and calcium chloride heat sink in proper proportions and soaking it at the reduction temperature (1223 – 1273 K) in flowing argon atmosphere, for sufficient time. The reduced mass is then leached with dilute acids to recover the metal powder.

Unlike the static bed reduction described above, in a bomb

process, highly exothermic reactions are conducted to prepare high melting metals in consolidated form. To achieve this objective many techniques have been evaluated in reactions releasing inadequate heat. These include: (i) preheating to ignition, (ii) additives acting as thermal boosters, and (iii) combination of both. The best reductant for the purposes just outlined is aluminium.

Carbothermic reduction to produce refractory metals has become a reality with major advances in vacuum technology. The reactions are performed in a high temperature-high vacuum induction furnace where the pelletized oxide-carbon or carbide-oxide charge is reacted in the solid state to yield carbide or metal. A precise control of charge composition and the reaction conditions is essential for obtaining pure metals having low residual carbon and oxygen contents. Adopting this process, complete flowsheets have been developed for the production of reactor grade niobium and capacitor grade tantalum metals.

Molten salt electro-winning processes for the preparation of refractory metals, particularly tantalum and titanium and rare earths like misch metal and cerium were extensively investigated. The metal compound (chloride, fluoride or oxide) is dissolved in a low melting eutectic salt mixture composed of two or more alkali or alkaline earth chlorides or fluorides. During electrolysis, the high melting rare metals are obtained as adherent dendrite deposits on the cathode (which is kept suspended in the fused salt) or alternatively if the adherence characteristics are poor, the metal is generated in the form of powder, in which case the cell itself is used as the cathode (and the anode is kept suspended). Tantalum and titanium have been electrodeposited in the dendritic and sponge forms by electrolyzing KCl-NaCl melt containing respectively potassium tantalum fluoride and titanium chloride as the functional salt. While for tantalum a centrally suspended metallic rod is used as cathode, for titanium a perforated metallic basket served as the cathode. Such electrode arrangement for multivalent titanium was found essential for separating the catholyte and the anolyte.

The molten salt electro-refining technique was perfected for the preparation of high purity metals like niobium, tantalum, vanadium, molybdenum and chromium from their aluminothermically reduced alloy form. More recently electro-refining technique was proven to be an effective mode for purification of calcium reduced hafnium. It has been possible to

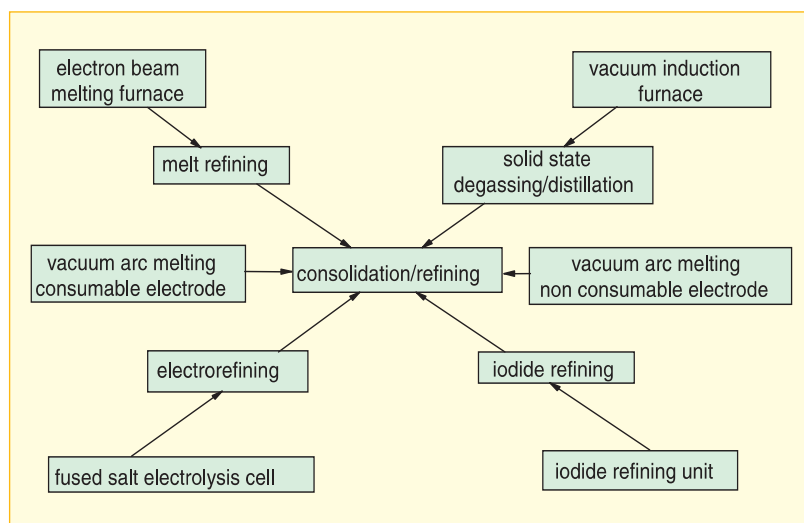
apply electro-refining for metal values of zircaloy scrap, and off-grade titanium sponge. Such purification technique was found suitable not only for clean scrap but also for scraps contaminated with other metals and alloys which cannot be directly used in conventional remelting.

Several new approaches in molten salt electrometallurgy were explored. A particularly useful method is electro-extraction. It is an extension of electro-refining wherein the anode is not an impure metal or alloy but a compound such as metal carbide, nitride and in some cases, sulphide also. All the refractory metals of group IV, V and VI were obtained by electroextraction. This technique along with others described has greatly expanded the effective options available for metal reduction/refining.

### Consolidation and Purification of Rare Metals

The reduced sponge metals and metal powders are required to be consolidated by melting or sintering prior to conversion to mill products. In some cases the melting or sintering operation refines the metal to an extent. The tolerable limits of impurities in rare metals are quite low. All the properties, which make these metals unique in comparison with other common metals are drastically impaired even by low levels of metallic and interstitial impurities. Therefore, great care and special techniques are employed in the refining operation.

Most of the purification methods for rare metals involve high temperature and vacuum. They include (i) vacuum melting, (ii) iodide refining, (iii) zone melting, and (iv) molten salt electro-refining. Majority of the metals are consolidated and refined by arc and electron beam melting procedures except beryllium,



which is consolidated, and to some extent refined, by vacuum induction melting and casting. In both these methods, crucible contamination is eliminated by carrying out the melting in water cooled copper crucibles.

Electron beam melting has, in fact, played a prominent role in its application to consolidation and purification of primary metals with widely different production history, and to preparation of metals with their finished purities meeting specific application requirements. Electron beam melting is effective and has been extensively used particularly in the production flow sheets of niobium and tantalum metals and their alloys. While vacuum melting is very effective in the purification of refractory metals it is not so with reactive rare metals like titanium, zirconium and hafnium. The so-called iodide refining has been found to be very effective in the refining of these metals.

A decomposition assembly now has been growing kilogram quantities of high purity crystal bars of zirconium, titanium and hafnium. In fact, as early as in the early 1970s, pioneering work was done on the production of crystal bar zirconium. The system has been used for the production of ultrapure zirconium/hafnium as required. The most recent version of the iodide refining unit is an automated system to ensure maintenance of controlled temperatures in the filament and feed and hence produce crystal bars in a reliable and reproducible manner.



Bar of zirconium crystal

Zone melting is essentially a purification process by repeated crystallization from the melt. In practice, two liquid-solid interfaces are produced for distribution of impurities by causing a relatively small molten zone to transverse the length of the bar of the charge. Many repetitions of the process lead to considerable purification even in cases where the distribution coefficient of the impurity between the melt and the solid is close to unity. The impurities that are more soluble in the solid, concentrate in the starting end. Zone refining in vacuum combines the benefits of conventional zone refining in a protective atmosphere, vacuum degassing and selective distribution of impurities.

## Thermodynamic Basis for Rare Metals Extraction

In the development of the process metallurgy of rare metals, the role of basic research, particularly thermodynamic investigations, is very significant. Thermodynamic data have come to the rescue in many situations either during the choice of process parameters or in explaining many of the system behaviour. Though the involvement of thermodynamic analysis is very extensive and pervades almost all stages of rare metals reduction, and refining, investigations concerning the vapour pressure and vaporization behaviours at elevated temperatures, solid solubility and phase diagram data have particularly been the main thrust areas for data collection and utilization. Investigations on metal-crucible interaction behaviour and decomposition processes are among the direct application areas for thermodynamic data.

Several processes have been developed based solely on the available thermodynamic data of the system concerned. While it is impossible to carbothermically reduce zirconium and hafnium oxides, a carbothermic reduction process consisting of reduction of niobium pentoxide with zirconium carbide or tantalum pentoxide with hafnium carbide respectively obtained the important master alloys zirconium-niobium and hafnium-tantalum. This scheme of reduction was worked out from theoretical considerations of the thermodynamic stabilities of carbides and oxides and the stabilities and vaporization behaviour of the sub-oxides of zirconium, hafnium, niobium and tantalum. Another example of major flow sheet development that was visualized from the thermodynamic properties of the concerned compounds, is found in the preparation of pure niobium and tantalum through their nitride intermediates. The comparative stability of niobium and tantalum nitrides with respect to the niobium and tantalum carbides at moderate temperatures and the complete instability of these nitrides (in contrast to the persistent stability of the carbides) at higher temperatures and vacuum conditions has made it possible to obtain the pure metals starting from the oxides by carbothermic reduction of niobium or tantalum pentoxide under a nitrogen atmosphere at 1773-1873 K to obtain the corresponding nitride followed by pyro-vacuum decomposition of the nitride, at 2273 – 2373 K under  $10^{-4}$  torr, to pure metal. In another investigation, the nitrides were obtained from nitriding of ferroalloys of the refractory metals, which were eventually decomposed to pure

metals at high temperatures in vacuum.

Continuing the tradition of translating thermodynamically consistent reduction and refining reactions to actual working process schemes, it was shown that use of silicon as a reducing agent results in a process that, besides being procedurally feasible has both technical and cost advantages. The process is based on the stability and volatility of silicon monoxide. The production of pure niobium and tantalum as well as metal silicides by silicon reduction was demonstrated to be attractive alternative to the existing process. The potential of using the stability and volatility of boron oxides was also demonstrated in the processes for preparation of borides and elimination of boron from refractory metal and alloy matrices by pyrovacuum treatments.

Apart from oxide processes, thermodynamic analysis was applied to reduction distillation type of processes involving fluoride intermediates. This was shown to be particularly useful for metals like vanadium that avidly pickup but seldom release interstitial impurities like nitrogen.

In addition to the above mentioned types of applications, thermodynamic analyses have extensively been employed in various pyrovacuum refining operations, leading to broader process options, successful process operation, improved yield, reduction in number of processing steps and similar enhancements.

## Recovery of Metals from Secondary Resources

When working on process development for the extraction of certain metals specifically required for nuclear energy applications, there are often situations where natural extension of the process to a co-occurring element or to a related element comes up. Most famous examples of this is the use of zirconium experience for titanium, that of niobium for the processing of tantalum, vanadium and the production of various ferroalloys of refractory metals by aluminothermic reduction. Considerable work has been done and significant contributions have been made in developing the processes for recovery of refractory metals such as tungsten, molybdenum, niobium, tantalum, vanadium and zirconium from a variety of indigenous secondary resources using indigenously manufactured equipment. Depletion and limited availability of primary sources, relatively large applications requirement and greater emphasis on environmental preser-



vation have led to increased pressure in using the secondary resources of these metals.

As compared with the historical development of the process metallurgy of common metals, there has been a more systematic and scientific approach to the chemical metallurgy of rare metals. This has been possible through many advances in analytical chemistry, physical chemistry, vacuum techniques, instrument and equipment development, and chemical engineering that have provided new technologies, and also through entirely novel metallurgical engineering designs. Basic understanding of chemical and metallurgical systems, phenomena and reactions has also vastly improved through progress in theory and experiments in rare metals extraction.

Growth, development and maturity in operating practice have marked the evolution of various process options taken up for investigations. Whenever required, the process development was pursued through the various stages and led to its logical conclusion - setting up of operating production facilities. DAE has been the nursery for rare metal extraction processes in our country.

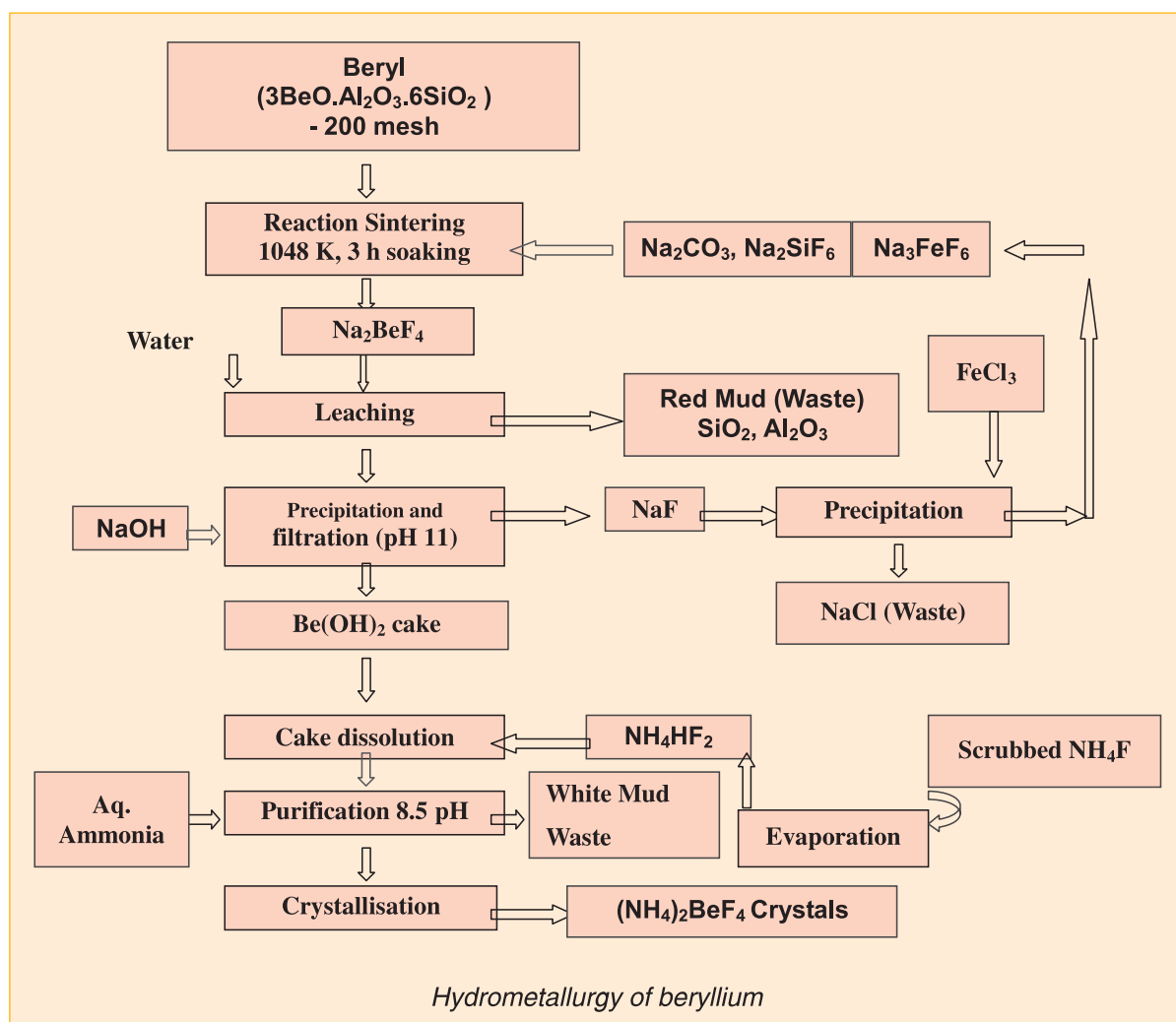
In the five decades of indigenous R&D in the preparative aspects of refractory and reactive metals and materials, DAE has embarked on the development of advanced materials processing techniques that range from super critical fluid extraction through self propagating high temperature synthesis to techniques and methods that empower composition and form control at the smallest building block level of materials.

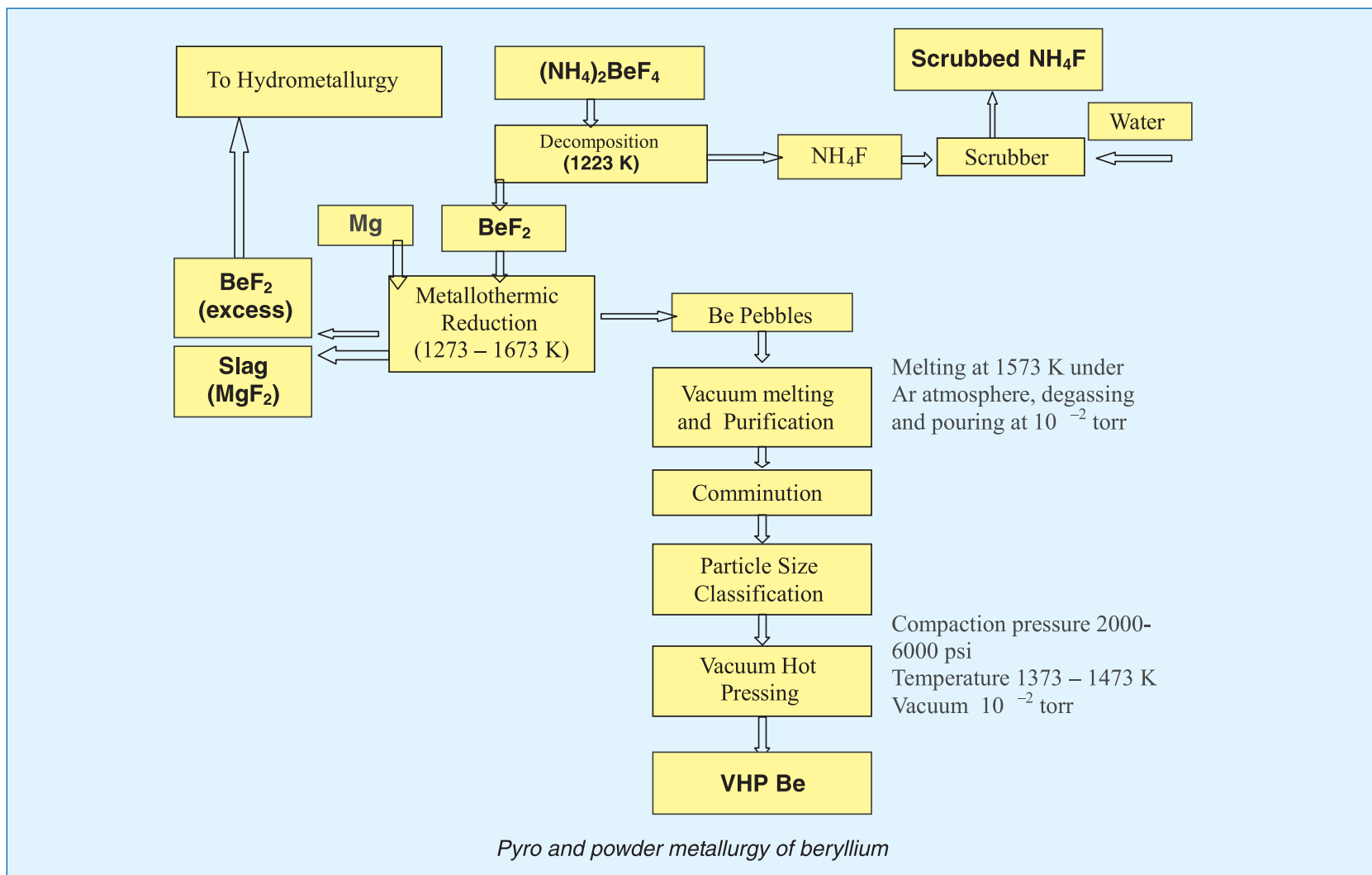
### Extraction and Powder Metallurgy of Beryllium

Beryllium metal has been called a 20<sup>th</sup> century enigma. It has unique combination of desirable physical, mechanical, thermal and

nuclear properties. It offers high modulus of elasticity and high strength to weight ratio. Its thermal properties include a high melting point, unusually large specific heat, good thermal conductivity and low thermal coefficient of expansion. This combination of properties imparts a very high dimensional stability to beryllium, which make it a material of choice for many applications in space programmes.

Nuclear applications of beryllium are based on its low neutron absorption cross section, high neutron scattering cross section and amenability for ( $\alpha$ , n) and ( $\gamma$ , n) reactions. These properties make beryllium a material of choice for moderator and reflector applications in nuclear reactors as also as a source of neutrons. Besides these, beryllium offers high transparency to X-rays. Beryllium has been used in India as a substrate for the elliptical mirrors for weather forecasting satellites, as windows in X-Ray tubes and nuclear detectors and for photo-neutron sources in combination with Sb<sup>124</sup>. Beryllium oxide is another important material known for its very high electrical resis-





tivity and high thermal conductivity. It is being used as heat sinks in high power electronic devices and has been chosen as moderator and reflector material for the Compact High Temperature Reactor (CHTR) being designed at BARC. Beryllium metal also finds extensive industrial applications in the form of copper – beryllium alloys, aluminum – beryllium alloys or aluminum – beryllium composites. Beryllium is a highly toxic metal and not amenable to easy extraction and conventional fabrication. The processing of beryllium and its alloys posed many challenges to metallurgists and designers.

To meet the demands of Be in the strategic sectors, a Beryllium Pilot Plant (BPP) was set up as a joint collaborative venture between departments of electronics, atomic energy and space, at Vashi complex of BARC in 1982. The integrated flow sheet for the extraction of beryllium from beryl and its consolidation by powder metallurgy was developed at a special laboratory set up for the purpose at BARC in 1968. The extraction

and process flow sheet is composed of several steps involving hydrometallurgy, pyrometallurgy and powder metallurgy.

At BPP beryl ore is processed to produce vacuum hot pressed beryllium blocks. These blocks are precision machined to different components by the Sintered Materials Machining Facility (SMMF). Beryllium metal pebbles, produced by magnesium reduction of beryllium fluoride, carry unreacted magnesium and small amounts of magnesium and beryllium fluorides as impurities. These pebbles are refined by vacuum induction melting in beryllia crucible. The furnace is indigenously designed and fabricated. At the time of setting of the BPP this was the first of its kind in the country. A major challenge in designing the furnace was the rotary coaxial vacuum compatible feed through meant for carrying the power and the cooling water to the induction coil.

## Powder Metallurgy of Beryllium

Beryllium metal is almost entirely processed through powder metallurgy. This is because as-cast beryllium contains large columnar grains and exhibits no ductility. The metal is therefore, extremely difficult to fabricate. Powder metallurgy has been found useful in this regard. For the production of beryllium powder, the vacuum cast ingot is turned using a lathe machine to produce swarf. The swarf is then ball milled to fine powder. Earlier, a four pot vibratory ball mill, with beryllium lined SS pots and tungsten carbide balls, was employed in the plant. This mill proved to be inadequate with respect to the quality and yield of the powder in specified grade. The mill has since been replaced successfully with an indigenously designed stirred ball mill.

The classifier used for recovering the desired fraction from the as-ground beryllium powder was designed by the project team. It is based on modified vortex principle. It is well known that the solid particles of an aerosol, on entering a cyclone, are subjected to radial and tangential forces. The classifier designed by the plant team has the provisions to vary these forces so as to cause particle size separation. The design of this classifier has been given to two companies in the corporate sector. A classifier was also built for IRE. This is being used for the classification of ceria powder used for the polishing shell of TV picture tubes. Very recently a classifier was designed and built for DMRL for the classification of iron powder to different size fractions.

Beryllium is a brittle material and requires considerable skill and experience in handling on the part of the machinist. It is dry machined owing to the high value attached to the scrap. The scrap can be largely recycled back at an appropriate step in the flow sheet for effective and efficient recovery of beryllium. SMMF set up by the Department of Space in the Vashi Complex is dedicated for the machining beryllium blocks produced by BPP. This facility has been set up according to ISO standards and is equipped with high precision machines and matching metrology instruments for qualifying the machined components for their dimensional and geometrical accuracy (linearity, circularity, cylindricity, sphericity and parallelism). The jigs and fixtures and cutting tools needed for machining have been developed indigenously. Various steps involved in complicated machining of beryllium have been mastered.

## Some of the components produced by beryllium facilities



*Beryllium Components of Rate Integrating Gyroscope*



*Beryllium Cluster for Inertial Sensing Unit-GSLV*

Beryllium and its compounds are highly toxic. The maximum allowable limits for air borne beryllium contamination are stipulated at  $1 \text{ mg/m}^3$  in the in plant air and  $0.1 \text{ mg/m}^3$  (averaged over 30 days) for the plant neighborhood. Liquid effluents from the plant are treated in-house to remove the beryllium and fluoride contaminations to below the stipulated limits of 0.1 and 5 ppm respectively. The technological process to achieve very low level of fluoride in the effluents has been developed and patented.

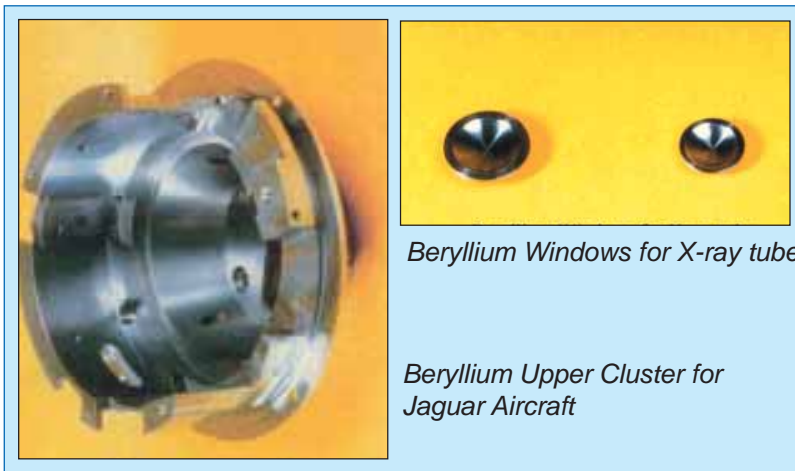
At BPP, initially copper-beryllium master alloy was produced by magnesium reduction of beryllium fluoride in the presence of copper in induction heated furnaces at 1673 K. In view of the high cost of production of the alloy in a small scale, production of alternative materials for specific applications is being explored including the production of aluminum beryllium alloys and development of technology for the preparation of nuclear



*Beryllium Scan Mirror major dimension : 340x210x20 mm*



*A Y- Thruster Bracket for INSAT-2C (Operational)*



*Beryllium Windows for X-ray tube*

*Beryllium Upper Cluster for Jaguar Aircraft*

grade beryllium oxide and its consolidation to shapes required for the CHTR programme.

The beryllium facilities have produced a number of components required for critical applications in the country's space and nuclear sciences programmes. Besides developing beryllium technology, BPP has also designed and built a number of special equipments related to powder metallurgy and thermo-vacuum treatment of materials. The performance of these equipments has been excellent and the designs are available for commercial exploitation.



## REACTOR CORE MATERIALS AND FUEL SUB-ASSEMBLIES

### Development of Automatic Spacer-Pad Welding Machine for PHWR Fuel Fabrication

Pressurised Heavy Water Reactors (PHWR) are fuelled by uranium dioxide in the form of pellets encased in zircaloy tubes and encapsulated to form fuel elements. For the 220 MWe PHWR reactors, nineteen numbers of such fuel elements are assembled to form a fuel bundle, such that one element is in the centre, six elements in the inner circle immediately around the central element and the remaining twelve elements in the outer-circle. In contrast, the 540 MWe PHWR reactors are designed to have a 37 element fuel bundle. The process of assembling the fuel bundle includes welding of tiny appendages called spacer pads on the periphery of each fuel element and bearing-pads on the periphery of the outer-circle elements only. The appendages ensure uniform passages for coolant flow around the surfaces of every element in the reactor.



*Integrated Appendage welding machine for 37 element PHWR Fuel — designed and fabricated in-house*

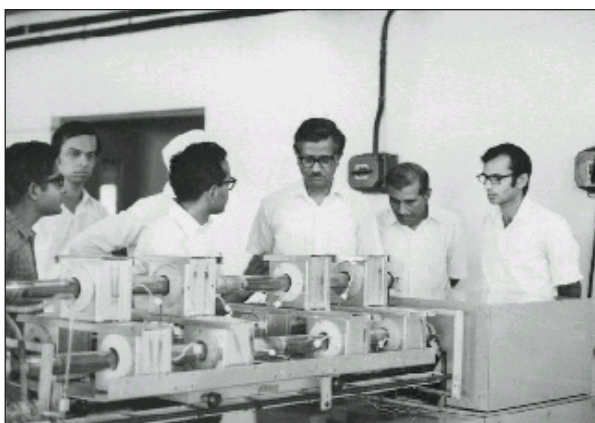
The spacer pads are very small precision components with two projections each of which are welded at a helix angle of 15 degrees at the center of the cylindrical periphery of each fuel element adopting the projection type of electrical resistance welding process. A reactor of 220 MWe capacity has a full charge of 3,672 fuel bundles. The number of spacer-pads welded for each 19-element fuel bundle is 72. The total number of spacer-pads welded for one full charge of the reactor

works out to be 2,64,384. Also, as a reactor operates and its fuel gets used up, the fuel bundles need replacement with fresh ones, which is of the order of one full charge in two years for every installed reactor. The quality of the welds should meet very stringent requirements of the nuclear industry with respect to their strength, oxidation, welding metallurgy, location and orientation accuracy, etc. The actual process of spacer welding on fuel elements involves several steps, viz., positioning the fuel elements, precise placement of the space pad on it, actuating the weld head to create the required electrode pressure on the spacer, providing an inert atmosphere of argon gas in the weld zone, passing the precisely controlled weld energy pulse, and indexing the element to facilitate welding of the next spacer. In meeting this huge requirement of welding spacer pads, while ensuring quality and reliability of every weld, automation of the process is found to be very essential. All these steps were earlier carried out on manually operated resistance welding machine using several switches, manual indexing plate etc. A welding machine with an indigenous microprocessor-based electronic controller to automatically weld the spacer-pads for PHWR fuel fabrication was designed, developed and put into regular production work. It has helped in reducing operator fatigue, improving quality and productivity and in giving consistent results.

Attachments of spacers/bearing pads onto fuel sheath by employing resistance welding techniques needed extensive research. This involved designing of specially coined components and standardization of their fabrication route; design and manufacture of special purpose equipment to carry out split spacer/bearing pad welding; standardization of process parameters, testing and qualification procedures etc. Continuous manufacturing of split-spacer fuel bundles is going on since 1986. Today, India is the only country employing resistance welding for appendage attachment which is safe, cost effective and is a superior process. Advanced countries like Canada, who are employing beryllium brazing for the same purpose, have acknowledged the superiority of resistance welding technology. It is pertinent to note that beryllium brazing involves use of highly toxic beryllium causing health hazard.



H.C. Katiyar briefing J.R.D. Tata at NFC



Dr. Raja Ramanna seeing zone refining facility in SMP. S. C. Jain, Balachandran, A. D. Damodaran, A. K. Taneja are also seen

### Development of Indigenous Designs, Fabrication and Automation in Fuel Element Fabrication

The very first indigenization effort in fuel plants began in 1974 by building a high temperature furnace for sintering for  $UO_2$  pellets. It was commissioned in the year 1975 and operated successfully for regular production for many years. Based on this design many more furnaces were built later.

Development of a process to attach split spacer/bearing pads on to the fuel sheath was the key factor in effecting change-over of fuel production from wire-wrap to split-wart design. A completely new process was adopted for this purpose. After successful development of the process and based on initial laboratory scale equipment, it was a challenge to conceive and build high capacity equipment that could fit into the already existing 100 tonnes per annum production line. Since imports were not possible the equipment needed were required to be built in-house. Resistance welded appendages being unique to Indian PHWR fuel bundles, special QC/QA procedures were required to be adopted for this process. The fuel development group

	19-element Bundle for PHWR 220	37-element Bundle for PHWR 540
$UO_2$ Pellet Diameter (mm)	14.30	12.20
OD of Cladding Tube (mm)	15.25	13.08
Wall Thickness (mm)	0.40	0.40
Length of Fuel Element (mm)	493.00	493.00
Wt. of $UO_2$ / Element (kg)	0.80	0.608
Wt. of $UO_2$ / Bundle (kg)	15.20	22.50
Wt. of Zircology / Bundle (kg)	1.40	2.00
Wt. of Fuel Bundle (kg)	16.62	24.50
No. of Components / Bundle		
Fuel Tubes	19	37
End Caps	38	74
Spacer Pads	72	156 (2 types)
Bearing Pads	36	54
End Plates	2	2
No. of Welds per Bundle	328	622
No. of Bundles required		
- Initial core	3672 (306x12)	5096 (392x13)
- Reload / annum	2400	4050

designed and built computer based weld strength testing units that became an important tool in statistically evaluating the strength of resistance welded joints.

In order to meet fuel requirements for the envisaged nuclear power generation programme, DAE embarked on expansion plans in the mid 80's. Owing to the restrictions imposed by advanced countries for the supply of critical equipment for sensitive applications, indigenous efforts had to be stepped up on war footing with the objective of meeting the delivery schedule of fuel bundles. This opportunity was well utilized in developing competence and self-reliance in manufacturing high-technology process equipment. In the indigenization programme, many Indian industries were encouraged to accept challenges of developing equipment that culminated in the manufacture of the majority of critical equipment for the first time in the country. The equipments developed include: microprocessor controlled rotary calcination and reduction furnaces, turbo-drying for ammonium di urinate, slurry extraction unit for uranium purification, high temperature sintering furnace, microprocessor

based end-cap welding machine for PHWR fuel elements, automatic spacer and bearing pad welding machines, PC based weld strength testing machinery for spacer/bearing pads, graphite coating equipment, vacuum baking equipment for PHWR fuel tubes, special purpose double-head turning machines for fuel tubes and fuel elements, automatic end plate welding equipment for PHWR fuel bundles, degreasing and cleaning systems with mechanized material transfer, equipment for automatic loading of  $UO_2$  pellets into fuel tubes, etc.

### Indigenous Efforts for the Development of BWR Components

Suitable vendors have been developed for the manufacture of tie plate casting (304 SS material) of intricate shape and for meeting the stringent specifications of castings. The tie plate castings are subjected to radiography, surface defects and dimensional accuracy qualification before machining to very close tolerances. The spacer grids in BWR fuel assembly are of a highly complicated design and of high cost and were earlier imported from USA, Germany & Japan. These have been substituted with zircaloy spacer sheet developed indigenously. A special welding machine was designed and fabricated in-house to weld the modified elements under a helium pressure of 2.5 kg/sq. cm. Regular production started from March 1981 onwards.

### Fast Breeder Reactor Component Facility at NFC

For the FBTR located at Indira Gandhi Centre for Atomic Research, Kalpakkam, production of fuel subassemblies for the first core and also for the subsequent charges had to be taken up. In the 70's it was decided to set-up such a facility at NFC. After completion of erection and commissioning of equipment and machinery, the FBTR facility went into production by 1980.

Core sub-assemblies for FBTR are high performance components which are put to severe operating conditions and hence it is imperative that a very high standard of quality, reliability and reproducibility be maintained in every aspect of fabrication. Unlike fuel assemblies of PHWRs and LWRs, FBTR sub-assemblies are component predominant. A fuel sub-assembly of FBTR, consists of as many as 511 machined components of 35 different types.

The various core sub-assemblies that were fabricated and supplied to reactor site well in advance of the scheduled date



*SS 316/D-9 hardware for fuel assemblies & core components for FBTR and PFBR*

include, steel reflector sub-assemblies, radial blanket sub-assemblies, nickel, reflector sub-assemblies, upper and lower axial blanket sub-assemblies and special subassemblies for irradiation experiments. A special mention must be made here that all these assemblies were fabricated with know-how developed in-house and fixtures/equipment built indigenously. With the completion of the design of core assemblies for 500 MWe PFBR developmental work for establishing fabrication flow-sheet for various types of assemblies which are more complicated than those of FBTR was initiated. NFC has already fabricated and supplied a bent assembly for handling tests that required innovative manufacturing techniques to simulate the irradiation induced bend and swelling in the assembly. Full-fledged PFBR fuel assemblies for hydraulic tests involving about 1541 components in single assembly have also been fabricated. Currently, the plant is engaged in the fabrication of other types of assemblies for type tests to generate data so as to validate and freeze the design of core assemblies. Towards the fabrication of these assemblies, all the necessary equipment were designed and built in-house.

Except for the indigenous-manufacture of blanket tubes, all the other core structural materials like 316M, 316L, nimonic, nickel, special spring wires etc., were imported for the first core mostly in the finished form. Presently all efforts are being made to indigenise the manufacture of critical components like fuel tubes, hexcans and other special materials like D9, required for both, FBTR and PFBR.



## CONTROL ROD MATERIALS

These materials have high ability to absorb neutrons (neutron poisons) and are fabricated in the form of rods. Control rods are distributed in the core of the reactor for controlling the rate of neutron chain reaction in the reactor. This is achieved by dynamically adjusting the depth of insertion of these rods into the reactor core. If the control rod is inserted to a deeper level, then a greater fraction of neutrons are absorbed, making them unavailable for the fission reaction in the fuel, thus controlling the rate of neutron multiplication factor and hence power. Thus, control rods can be used to shut down or to restart the reactor. Boron, cadmium, gadolinium are conventionally used control rod materials owing to their high neutron absorption cross-section. The neutron absorption properties of an element also depend strongly on the isotopic number. The thermal neutron absorption cross-section for  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes are 3837 and 0.005 barns respectively, whereas natural boron has an absorption cross-section of 752 barn. For 1 MeV energy neutrons, the absorption cross-section is 1 barn for natural boron.

### Boron Carbide

Boron carbide ( $\text{B}_4\text{C}$ ) is used in the nuclear industry as neutron absorber and shielding material due to the high neutron absorption cross section of boron atoms. While pure oxides and in some cases halides of reactive and refractory metals are usually obtained as end products of separation operations, carbides and nitrides are usually prepared as necessary process intermediates for eventual conversion to a metal or an alloy. These refractory metal compounds as well as some of the borides and silicides are by themselves important end products for many applications. This aspect first came into focus in the early 1980s when boron carbide was required for a variety of reactor control and neutron shielding applications.

Instead of going through the conventional oxide-carbide reaction in a compacted mixture of reactants, a reaction scheme similar to the one commercially used for silicon carbide manufacture was chosen for the production of boron carbide as well. The process and a self-resistance heated reactor was standardized for the production of boron carbide that yielded 10-15kgs of carbide per batch. This formed the basis of all subsequent activities built around boron carbide, including its fabrication as the composites boral, and bocarsil, and products such

as hot pressed blocks of boron carbide. The products were extensively used at various operations within DAE for over three decades. The original processes have been in recent times adopted, upgraded to prepare new materials such as enriched boron carbide and materials incorporating enriched boron. Along with boron carbide, borides of refractory metals and the rare earths have also been prepared and consolidated for various specific end applications.

### Boron Carbide Control Blade for TAPS

Control blade for the boiling water reactor at TAPS is a four meter long assembly of cruciform cross section, fabricated mostly out of stainless steel and boron carbide powder. The blade is positioned in between four channels that cover the fuel bundles. Each reactor contains 69 blades. The blades are used for controlling neutron flux by gradual axial movement or for shutdown by rapid scram insertion.

The technology development of TAPS Control Blade was taken up in 1976 and prototype testing was conducted between 1977 and 1983. The prototype control blades were cleared by DAE Safety Review Committee for loading in TAPS in 1983. The first two blades performed exceedingly well in the reactor and lasted its full operation of around seven years. The technology development included design, development of manufacturing drawings, usage of appropriate NDT techniques to generate component and assembly dimensions with precise tolerances, material selection for each of the 24 components constituting the blade assembly. This work also comprised of development of  $\text{B}_4\text{C}$  powder, vibro-compaction techniques to achieve required density, standardization of different welding techniques, procedures and their qualifications, various QA and QC plans etc. Since 1983, control blades to TAPS have been continuously fabricated.

### Technology Development for Boron Enrichment, Elemental Boron and Boron Carbide Production

In FBTR and PFBR boron Carbide ( $\text{B}_4\text{C}$ ) having different levels of enrichment in  $^{10}\text{B}$  are used in control rods. The control rod material for FBTR requires 90% of  $^{10}\text{B}$  whereas for PFBR requires 65% of  $^{10}\text{B}$ .

Though France, US, Russia and China are engaged in production of enriched boron carbide, no country is willing to ex-



port this strategic material. US, Russia and China are enriching  $^{10}\text{B}$  using distillation of DME- $\text{BF}_3$  complex whereas France is producing  $^{10}\text{B}$  by ion exchange chromatography. India has developed an indigenous technology based on ion exchange chromatography.

### Enrichment of Boric Acid

The resin in ion exchange column is loaded with natural borate ions either as boric acid or any of its complexes. The process of displacement chromatography is used for enrichment of  $^{10}\text{B}$ . Due to flexibility of operation in ion exchange process and ease of availability of feed material, studies have been undertaken at to enrich  $^{10}\text{B}$  isotope of boron using ion exchange chromatography. Borate band is moved from one column to the other in a battery of ion exchange columns. During the band movement, the rear end of the borate band is enriched in  $^{10}\text{B}$  isotope due to its higher exchange affinity compared to  $^{11}\text{B}$  isotope. The exhausted resin in chloride form is then regenerated to hydroxide form and put back in service to facilitate continuous band movement. The product is eluted out of the band as enriched boric acid solution. A plant was designed and commissioned in 2001 to produce enriched boron  $^{10}\text{B}$ . After operating the plant for 10 months, an enrichment of 40% could be achieved. The depleted portion of the borate band and loading the fresh natural boric acid to increase the inventory of  $^{10}\text{B}$  in the band resulted in an enrichment of 65% in  $^{10}\text{B}$ . With this the technology for achieving the desired enrichment for PFBR requirements has been demonstrated.

### Pilot Plant for Exchange distillation for Enrichment of $^{10}\text{B}$ isotope

A pilot plant of 500 gallons/year capacity based on chemical exchange of boron trifluoride ethyl ether complex and boron trifluoride gas was set up and operated. The product was converted to boron trifluoride-calcium fluoride for use in neutron counters. The exchange distillation process is basically a chemical exchange between  $\text{BF}_3$  gas and diethyl ether- $\text{BF}_3$  complex and that in which distillation is used to obtain chemical reflux. The diethyl ether- $\text{BF}_3$  complex is dissociated in the vapour phase and on cooling  $\text{BF}_3$  and ether recombine to form the complex. The chemical exchange of isotopes takes place between  $\text{BF}_3$  in gas phase and complex in the liquid phase.

The exchange process is carried out in packed columns where  $\text{BF}_3$  gas and the complex are contacted in the counter current manner. The reflux is obtained by conventional distillation technique. The distillation is carried out under partial vacuum to reduce decomposition of complex. The column is operated at a condenser pressure of 20mm Hg abs. The reboiler temperatures are controlled between 75-80°C. The product from this plant was made available for internal use and also supplied to ECIL, Hyderabad for neutron counters.

### Conversion To Elemental Boron

There are many methods, such as i) carbothermic reduction of boric acid / boron anhydride ii) magnesiothermic reduction of boron anhydride iii) thermal decomposition of a mixture of  $\text{BCl}_3$  and  $\text{CCl}_4$  in  $\text{H}_2$  d) reaction between  $\text{BCl}_3$  and  $\text{CH}_4/\text{H}_2$  gas mixture etc., available for the preparation of boron carbide. The carbothermic and magnesiothermic reduction processes are commercial processes for the large scale fabrication of boron carbide. These methods employ very high temperatures (> 2273 K) for the reduction process and boron loss due to vaporization of volatile boron compounds is very high. Hence, these two methods cannot be employed for the production of enriched boron carbide. Production methods involving the halides of boron are also not suitable for the large-scale production of enriched boron carbide due to very high cost of boron halides and the complications involved in the operations during handling and storage of these compounds. To avoid the losses of enriched boron, an alternate technology has been developed for the fabrication of boron carbide. In this process, boron carbide is prepared in two steps. In the first step, elemental boron is obtained from  $\text{KBF}_4$  by electrolysis of fused salts. In the second step, boron carbide is synthesized from its constituent elements. The loss of boron is minimal in this route. Based on the technology developed at BARC, a facility was set up at IGCAR to demonstrate feasibility of production of elemental boron from boric acid. Six boron production campaigns (each with specific objectives) were carried out at IGCAR during 2003-2004. All the process parameters required for production of Boron have been optimized. This facility has provided necessary inputs for setting up of industrial scale manufacturing facility by Heavy Water Board.

## Conversion to Boron Carbide and Fabrication of Boron Carbide Pellets

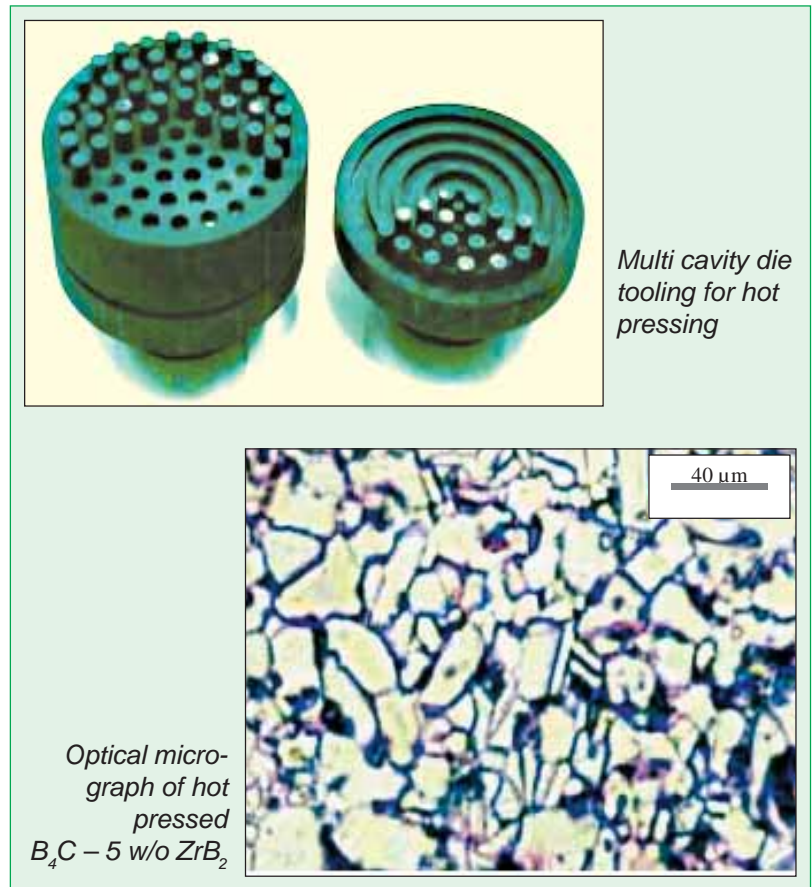
Boron carbide is synthesized from elemental boron by reacting it with carbon at high temperature in a vacuum of  $10^{-5}$  m bar. The product is a loosely sintered pellet, which is crushed, milled, and micronised to a size of few microns. The fine powder is then purified by chemical means to remove the contaminants picked up during the powder preparation steps. The purified powder is cold pressed to the required shape and then hot pressed at a temperature of 2073 to 2273 K in specially designed graphite dies to obtain dense pellets. These pellets then undergo mechanical processing to achieve the close tolerances and surface finish. The pellets of specified density and surface finish are used in the control rods for fast breeder reactors.

## Fabrication of Ceramic Control Rod Materials by Hot Pressing

Boron containing ceramics (boron carbide and borides) are difficult to sinter by conventional sintering approach without a sintering aid. Temperature of above 2273 K is needed to achieve close to the theoretical density. The desired density, and the microstructural control (grain and pore size and their distribution) in these materials are achieved by adding sintering aid, grain growth inhibitor or pore-formers. However, for use in nuclear reactors, compositional control is very important and certain additives may not be desirable. In view of this, fabrication by hot pressing was developed as a useful tool for fabricating control rod materials (borides and carbides) with desirable density and microstructure. It may be mentioned here that borides and carbides have good electrical conductivity in general and hot pressed material can be electro discharge machined to give complex shapes.

Hot press with graphite hot zone and graphite die is ideally suited for processing of carbides and borides where carbon contamination is not a critical issue. Hot pressing of boron carbide and titanium diboride based materials were carried out using various single and multi-cavity dies. Vacuum hot pressing parameters – pressure, temperature, die lubrication, pressing time etc. were optimised to achieve the desired density.

Hot pressing was also found to be a very useful tool in producing boron carbide - zirconium diboride (in-situ prepared) composite with controlled porosity. In this case boron carbide



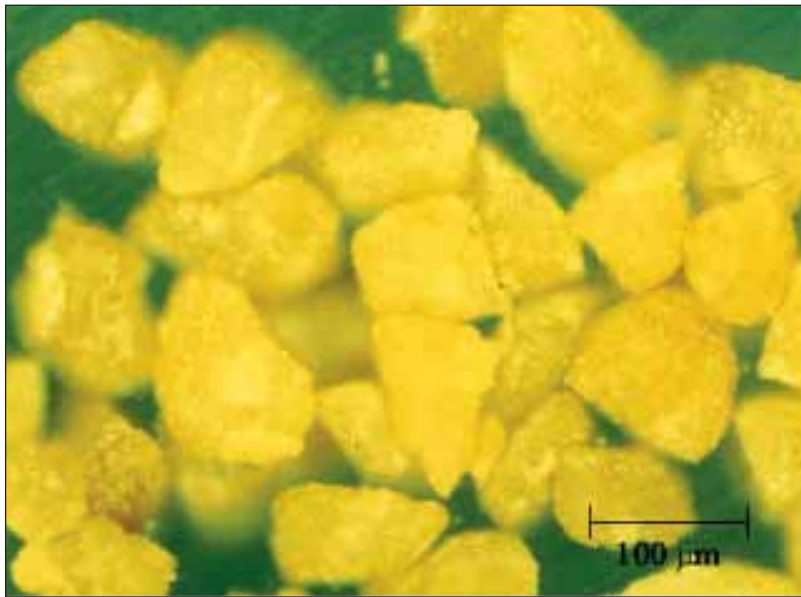
and zirconia powder mix is used as the charge material for hot pressing. Twinned grains are typical feature of hot pressed boron carbide. Hot pressing of titanium diboride based material (TiB<sub>2</sub>-CrB<sub>2</sub>-MoSi<sub>2</sub>) has been carried out at a temperature of 2073 K and at 30 MPa pressure. Density close to theoretical density could be achieved.

## Development of Gadolinium Aluminate Based Ceramic for Nuclear Applications

Compared to boron, the absorption cross sections of rare earth elements like gadolinium and samarium are much larger. The absorption cross section of thermal neutrons is about 40,100 barns for samarium-149 and about 2,54,000 barn for gadolinium-157 isotopes. Also, the absorber materials based on boron carbide as well as boron steels undergo large radiation induced damage in a nuclear reactor caused by (n,α) reactions with B<sup>10</sup> isotopes and subsequent swelling of the control elements occurs due to formation of helium gas. Service life of an absorber material is therefore, largely governed by the radiation stability of the material rather than the decrease in the neutron absorption efficiency. In the case of boron carbide, the

irradiation swelling and its subsequent interaction with cladding are the major causes of clad failure. Carbon diffusion from  $B_4C$  into stainless steel cladding also causes sensitization and hence subsequent cracking.

Control rods based on  $(n, \gamma)$  absorbers are therefore promising for thermal reactors as they circumvent swelling problems associated with absorbers based on  $(n, \alpha)$  reactions. Extensive study of these neutron poison materials has also therefore been carried out. Gadolinium has a very high thermal neutron capture cross section for  $(n, \gamma)$  reaction and the resultant reaction product has a very low capture cross-section. This element is therefore, used as a “burnable” poison in the nuclear reactors to control the reactivity of fresh reactor fuel assembly. Thus, the production of this material is of importance. A flow sheet was developed for the production of gadolinium aluminate and gadolinium aluminate-alumina composite powders on a mass scale. With the help of computer simulation and modeling, and powder granulometry, powders with predetermined gadolinium densities were obtained.



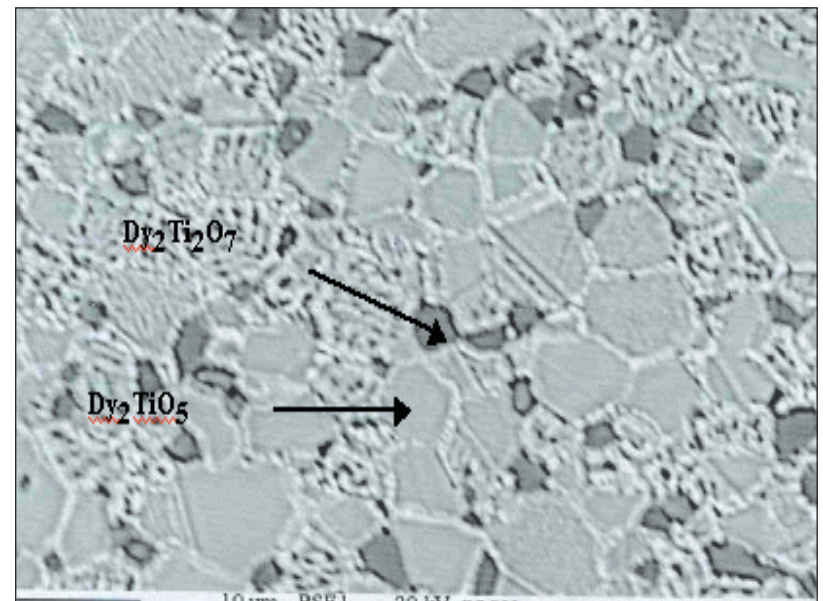
Gadolinium aluminate powder product produced through mixing and calcination route

### Development of Dysprosium Titanate Based Ceramics

Ceramics based on  $Dy_2TiO_5$  (dysprosium titanate) exhibit insignificant radiation swelling - high structural and volumetric stability, good corrosion resistance properties in water at 573 K, no interaction with cladding at temperatures as high as 1273

K and can be easily reprocessed resulting only in non-radioactive waste. All the daughter product  $(n, \gamma)$  reactions with dysprosium exhibit high absorption cross-section for thermal neutrons. All these radionuclides have a low gamma activity and a short half-life period.

The binary phase diagram of  $Dy_2O_3 - TiO_2$  shows two stable line compounds. These are dysprosium titanate ( $Dy_2TiO_5$ ) and dysprosium dititanate ( $Dy_2Ti_2O_7$ ).  $Dy_2TiO_5$  has three polymorphs. The low temperature orthorhombic phase transforms into hexagonal phase at a temperature of  $\sim 1623$  K, which on further heating converts into the fluorite phase at  $\sim 1953$  K. Of these three phases, the high temperature fluorite phase exhibits minimum radiation swelling.  $Dy_2Ti_2O_7$  has a pyrochlore structure, which is reported to transmute, under irradiation into a fluorite structure. For control rod applications, a composition in the two-phase field is therefore chosen with a resultant need to stabilise the high temperature cubic (fluorite) phase of  $Dy_2TiO_5$  at room temperature. This has been achieved through doping the  $Dy_2O_3 - TiO_2$  mix, followed by controlled calcinations. For



Backscattered Secondary Electron image of  $Dy_2TiO_5 - Dy_2Ti_2O_7$  ceramic sintered at 1873 K for 4 h

control rod applications in thermal reactors, dysprosium titanate is used both in pellet (density 3.6 g/cc) as well as in vibro-compacted powder form (density 4 –5 g/cc). The dysprosium titanate pellets produced by sintering at 1873 K yielded a density of 7 g/cc.



## Structural Materials

### Development of Zirconium Alloys for PHWRs

In PHWR, neutron economy becomes an important consideration in materials selection, since the natural  $\text{UO}_2$  fuel contains only 0.7% of fissile  $^{235}\text{U}$  atoms. Thus the cladding metal must possess low neutron absorption cross-section and must also be as thin as possible, consistent with adequate mechanical strength and with due allowance given for corrosion by fuel and coolant. On the basis of low neutron absorption cross section, one is limited to the use of only one of the following materials, namely, aluminium, magnesium, zirconium, beryllium and graphite. Out of the above, zirconium is the most preferred for power reactors because of its high melting point, good corrosion resistance in high temperature water and adequate high temperature strength.

Zirconium based alloys are the natural choice for both fuel element cans and in-core structural components such as pressure tubes, calandria tubes, garter springs etc. in the water cooled thermal reactors. The general requirements for these components include low thermal neutron absorption cross section, adequate strength, ductility and toughness at ambient and reactor operating temperatures. They also need to possess good corrosion resistance, low hydrogen absorption, long-term dimensional stability in irradiation environments, compatibility with fuel and coolant under service conditions, good heat conductivity and resistance to fracture. Pure zirconium undergoes uniform surface oxidation in high pressure water at 573 K. After a certain time interval, however, film cracking occurs leading to breakaway corrosion. It was found that the presence of impurities like nitrogen, carbon, aluminium, titanium and silicon, are associated with the above phenomenon. Further, it was noticed that additions of iron, chromium, nickel and tin, combined with restriction of nitrogen content reduces the tendency for film cracking. This led to the development of zircaloy-2 alloy, with 1.5% Sn, 0.12 % Fe, 0.1% Cr and 0.05 % Ni. Zircaloy-2 was widely used as clad, wrapper, pressure tube (PT) and calandria tube (CT) materials for PHWR. The major problems associated with this alloy are hydriding, stress corrosion cracking and irradiation creep. Hydriding can result either from attack by coolant or by reacting with the moisture in the fuel. Since nickel is known to increase the hydrogen absorbing tendency in zirconium,

zircaloy-4(1.5Sn –0.18-0.24Fe, 0.1 Cr, Ni<0.007) in which the hydrogen absorption rates are reduced to about half of that in zircaloy-2 have been developed for clad applications.

The requirements for pressure tube alloys differ from those for fuel cladding, largely because of the fact that an improvement in the strength of the material can significantly reduce the quantity of parasitic material within the core and that the pressure tube, unlike the fuel cladding, is expected to have a long service life preferably extending up to the design life of a reactor. Pressure tubes being the final pressure boundary containment structures in PHWRs, their integrity is to be maintained during reactor operation and safety demands that leak before break (LBB) criterion is met with. During service, all the zirconium alloy core components in general and pressure tubes in particular are subjected to very slow aqueous corrosion, hydride induced embrittlement and radiation damage. Zr-Nb based alloys are known to exhibit superior irradiation creep and hydriding resistance compared to zircaloy-4. Zr-2.5Nb is a precipitation hardened alloy and thereby the irradiation creep rate is significantly low. Also Zr-Nb alloys show slower hydrogen pick up rate, resulting in lower build-up stress around the blisters. Crack initiation is therefore delayed. Zr-2.5Nb alloy has therefore been chosen as the construction material for pressure tube and calandria tube of PHWR's under construction. India has indigenously developed zirconium production technologies and NFC is producing components of zircaloy-2, zircaloy-4 and Zr-2.5Nb.

In PHWR systems the various zirconium products are used in the form of tubes either to clad the fuel or to contain the pressurized heavy water coolant. The structural components like fuel tubes, pressure tubes and calandria tubes are exposed to highly aggressive environments during reactor operation. The main factors responsible for shortening the life of in-core components are radiation damage, in-reactor creep and growth, corrosion and hydrogen pick up during service life. Therefore, materials used for manufacturing these components must meet stringent requirements of various properties in order to perform reliably in nuclear reactor environments.

Calandria tube is exposed to lower temperature and lower stress compared to clad and PT and hence excessive deformation and creep is not of much significance. But radiation growth does pose some concern. Garter spring possesses high



## Coolant tubes used in various PHWR reactors

<u>REACTORS</u>	<u>TYPE OF PRESSURE TUBES</u>
MAPP-1	DRAWN Zr-2 TUBES
MAPP-2	PILGERED Zr-2 TUBES
NAPP-1&2	
KAPP-1	
KAPP-2	PILGERED Zr-2.5% Nb TUBES
RAPP-3&4	
KAIGA-1&2	
REPLACEMENT CHARGES FOR RAPS2, MAPS-2 & FRESH CHARGES FOR TAPP 3&4	
	PILGERED Zr-2.5% Nb TUBES FROM QUADRUPLE- MELTED INGOTS & WITH IMPROVED CHEMISTRY

strength and is subjected to complex loading at relatively lower temperature. Due to exposure to relatively lower temperature, hydrogen pick up is not of concern. The major concern for garter spring is their displacement from their designed loca-



End view of coolant channel assembly of pressurized heavy water reactor.

“... During my tenure as the Director, National Metallurgical Laboratory, Jamshedpur, I had the good fortune of overseeing collaboration in the research projects concerning toughness degradation of Zr-Nb alloys and fracture toughness evaluation of SA333 steel for earth-quake resistant piping. Besides, DAE generously contributed and participated whole-heartedly in the Component Integrating Evaluation Programme (CIEP) of the NML. The many stimulating interactions we had with senior scientists of IGCAR including Dr Baldev Raj, the present Director, were of immense help to us. IGCAR had even agreed to transfer one of its scientists to NML. This interaction had helped in the development of Non-Destructive Testing methodology at the NML. The fruitful and productive interaction continues today also.

As a teacher, I was involved in the supervision of the doctoral theses of young scientists from BARC. My students have had the privilege of interacting with senior scientists of DAE and used the extensive facilities available at BARC, IGCAR, CAT and other centers. We had the privilege of receiving aid from BRNS in order to conduct advanced scientific research.

Many of the faculty members of our University are continuing to interact with the eminent scientists and staff of DAE. We hope that these interactions will pave the way towards establishing more facilities on our campus. The role of DAE in promoting academic excellence at the Universities is outstanding...”

**Prof P.Ramachandra Rao**

Vice-Chancellor,

Banaras Hindu University, Varanasi

tion, which is also greatly reduced by employing tight fit springs. Moreover, these components are not the final pressure boundary containment structures. The pressure tube poses the major challenges for PHWR safety.

## UO<sub>2</sub> FUEL ASSEMBLIES & Zr- ALLOY CORE STRUCTURALS FOR PHWR 540 MWe AT TARAPUR (TAPP 3&4)



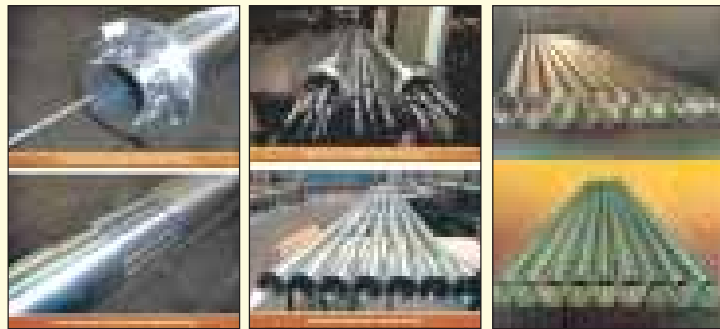
### FUEL CORE

- No. of Zircaloy 4 Clad 37-Element Fuel Assemblies (13x 392) ..... 5096
- Total UO<sub>2</sub> the Core ..... 110 Tons
- Total No. of Weld Joints in the Full Fuel Core ..... 31,69,712



**Electricity (kWh) from One Fuel Assembly**

**..... 9,26,000 units**



### ZIRCONIUM ALLOY CORE STRUCTURALS

- No. of Zircaloy 4 Seamless Calandria Tube ..... 392
- No. of Zr-2.5% Nb (Quadruple melted) Coolant Tubes ..... 392
- No. of Zircaloy 4 Reactivity and Shut-off Devices ..... 108  
(LZC, VFU, HFC, LPIT Assemblies)

### Hydriding and Stress Corrosion Cracking of Zircaloy

As mentioned previously, the two main life-limiting factors associated with fuel clad tubes are hydride embrittlement and iodine induced stress corrosion cracking (SCC) as a result of pellet-clad interaction.

Excessive hydriding could lead to performance limiting embrittlement. The extent to which the hydrides embrittle the clad also depends on the orientation of the hydrides. Formation of radial hydrides is an undesirable situation as it greatly reduces the ductility while circumferentially oriented hydrides have only marginal effect. Crystallographic texture has therefore an important influence in determining the orientation of hydrides. For a favourable hydride orientation, it is necessary that the alpha grains of zircaloy be oriented with the basal plane normals close to the radial direction. The development of texture is influenced by the strain history of the cladding tubes during fabrication. Careful optimization of process parameters at NFC involving cold pilgering to final dimensions, has led to the development of clad tubes with desired texture.

Though hydriding has been considered as the problem mainly with the fuel cladding, a few hydriding failures of pressure tube have been reported in Canadian reactors. The dislocation of the spacer spring associated with irradiation creep, can result in contact between the pressure tube with the cooler calandria tube. This can lead to migration and concentration of hydrogen in the cooler part of the pressure tube. Hydrogen in excess of solid solubility leads to formation of hydride precipitates, which makes the host zirconium matrix brittle. In zirconium alloys, two forms of hydride embrittlement have been recognized - gross and localized. The latter is an insidious failure mechanism in which damage accumulation takes place within a small region before any catastrophic failure may occur. The gross embrittlement requires certain minimum volume fraction of hydride phase, and it results in overall reduction in tensile ductility, impact and fracture toughness. Localized embrittlement is caused by hydrogen migration in the material under the concentration gradient, stress gradient and thermal gradient towards a localized region. In the presence of a thermal gradient,



*Graphite coating facility at NFC*

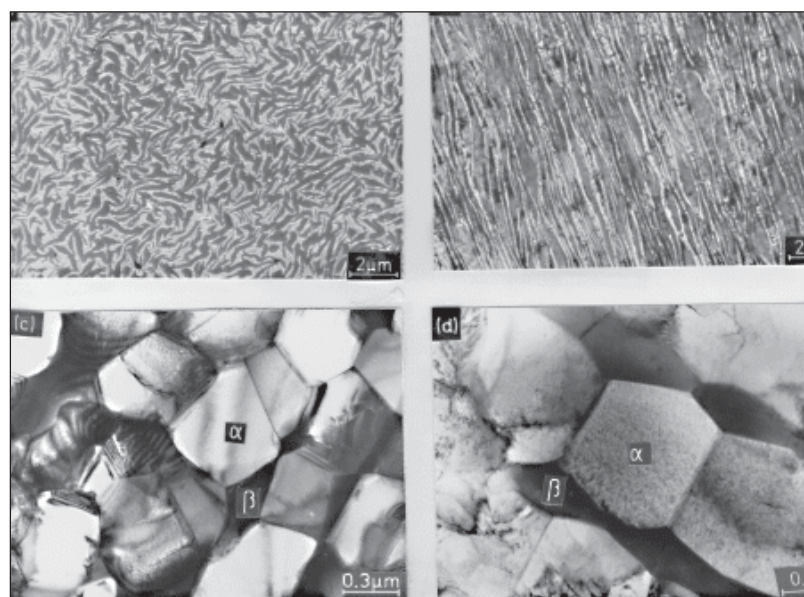
hydrogen migrates down the temperature gradient. Once the local solid solubility is exceeded, hydrogen precipitates out as hydride at and around the low temperature spot. Since transformation of zirconium metal into hydride is associated with an increase in volume, a bulge appears on the surface at the cold spot. This hydride bulge, due to its appearance, is called hydrogen blister. Though the formation of a single blister does not violate the LBB criteria of the pressure tube design, an array of blisters may form a crack of a length more than the critical crack length required for the catastrophic failure. Parameters like fracture toughness, threshold stress for reorientation of hydrides, blister formation threshold, critical depth for formation of cracked blister, delayed hydride cracking velocity, threshold stress intensity factor for DHC initiation are used for assessment of fitness for service of the pressure tubes. And if no preventive / corrective measures are taken, such crack may grow beyond the critical crack length required for unstable crack growth, which, in turn, might lead to catastrophic failure of the pressure tubes.

Stress corrosion cracking is also one of the important problems associated with clad tubes. This occurs when a fuel element, that has been exposed to prolonged irradiation at relatively low power, has its power increased. The resulting thermal expansion of the fuel stresses the cladding while fission product iodine released from the fuel is the likely corrodant. This problem has been solved by incorporating a thin layer of graphite on the inner surface of the cladding. After carrying out considerable developmental work at NFC the production

process for graphite coating of zircaloy tubes was standardised. An automatic coating equipment has been designed and fabricated with a high capacity vacuum backing unit. With these equipment the graphite coating process could be taken up on a production scale and it has become a part of the flow-sheet since 1990.

### **Fabrication of Zr-Nb Tubes**

India occupies a distinguished position among countries that have developed the total technology for processing, fabrication, characterization and use of zirconium alloy components in the nuclear industry. While zirconium alloys have proven to be successful in their designed usage, a desire for longer lifetime of components and increased duty cycle puts more demand on material performance. This demand has led to more in-depth studies of phenomena associated with zirconium alloy composition, development of fabrication techniques and to the evaluation of newer zirconium alloys for critical applications. Although zircaloy-2 was used as a pressure tube material in the very early versions of CANDU- PHWRs, there has been a mounting evidence that these zircaloy-2 tubes showed accelerated oxidation and hydrogen-up take over longer exposures in reactors. These led to the development of Zr-2.5 Nb alloy. Developing a new zirconium alloy involves several important steps: (i) the influence of controlled additions of interstitial and substitutional alloying elements for optimum



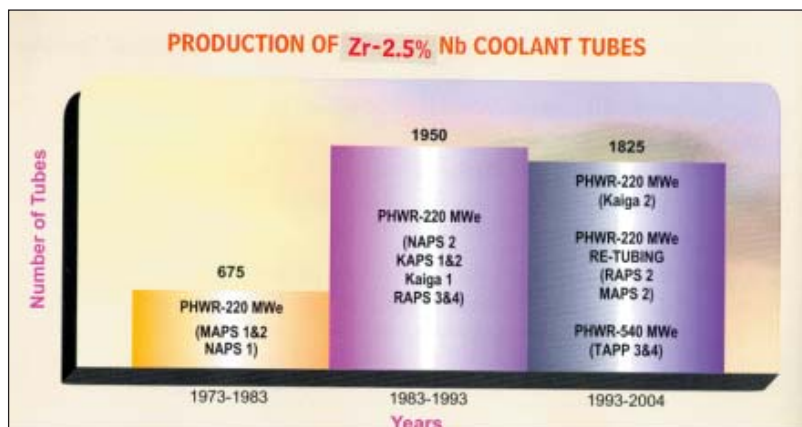
*Scanning and transmission electron micrographs of hot extruded Zr-2.5Nb pressure tube material in transverse and axial direction*



properties of the alloy, (ii) for chosen systems the range of possible metallurgical treatments has to be explored, and (iii) the problems concerning fabrication of these alloys to the required reliability and reproducibility have to be assessed and solved. With these points in view physical and mechanical metallurgy of a range of zirconium and its alloys have been studied in detail after various thermomechanical treatments. Based on the extensive development work done, a fabrication route was evolved for the production of thin walled, larger diameter tubes through seamless route. Advanced facilities to manufacture seamless tubes with close dimensional tolerances, with required quality and stringent mechanical properties were established. It was found that the fracture toughness of Zr-2.5Nb pressure tube alloy can be improved substantially by reducing the level of trace element impurities like hydrogen (from 25ppm to 5ppm), chlorine (from >2.5 ppm to 0.5 ppm), carbon and phosphorous. Such refining is achieved by multiple consumable vacuum arc melting. It was demonstrated that such purity can be routinely achieved by quadrupole vacuum arc melting practice at NFC. These are very significant developments since the reduction in trace elements give a substantial increase in the coolant channel life.

The list of various structural materials produced at NFC include seamless Zr-2% Nb pressure tubes for PHWR, seamless zircaloy-4 calandria tubes for PHWR, Zr-2.5%Nb-0.5%Cu garter springs for PHWR, reactivity control mechanism components for PHWR and zircaloy-4 square channels for BWR

These structural materials demand very strict control during fabrication to meet the stringent properties with respect to chemistry, mechanical properties, soundness and dimension. Components for the reactivity control are most critical and involved. Fabrication of these components is done in a number of stages



and finally assembled by welding. The number of components in case of 540 MWe is 2.5 times that in a 220 MWe reactor. During the last three decades, a number of zirconium alloys and components have been successfully manufactured and utilized in all the 14 operating water-cooled reactors in India.

### Cold Reduction of Large Diameter Thin Wall Tubes

Normally large diameter thin wall tubes are rolled in cold pilger mills using 2 roll dies. NFC has designed both rolling and auxiliary toolings for 150 VMR cold pilger mill and successfully rolled tubes with outer diameter to wall thickness ratio of around 100. This development resulted in successfully producing calandria tubes for PHWRs, which were earlier fabricated by seam welding process but are now produced by seamless process giving better integrity and uniform stress during expansion of mouth ends and subsequent rolling of joints in the reactor.

This innovative seamless pilgering process developed has resulted in achieving superior texture and consequent mechanical properties and dimensional tolerances over long lengths. NFC has also recently manufactured seamless zirconium alloy calandria tubes and coolant tubes for the PHWR-540 MWe at Tarapur. The PHWR 540 is the first in the series of 500 MWe type PHWR units in the country. Each PHWR 540 core has 392 co-axial assemblies of zircaloy-4 calandria tubes and Zr-2.5% Nb coolant tubes inside which the uranium fuel assemblies are loaded. Such long and thin walled seamless calandria tubes have been manufactured for the first time in the world.

150 VMR Pilger Mill







*Seamless calandria tubes for TAPP-3*

### **Development of Rolled Joints for PHWRs**

The coolant channels of Indian PHWRs, which house fuel assemblies, consist of zirconium alloy pressure tubes, connected to martensitic stainless steel end fittings at each end by rolled joints. The pressure tube forms the in-core component of the coolant channel. The end fitting provides connections to various interfacing systems i.e. primary heat transport feeder pipes, fuelling machine and annulus gas system bellow assembly.

The current generation of reactors use Zr-2.5 % Nb as pressure tube material as this material has higher strength and lower deuterium pick up rate. Since the Zr-2.5 % Nb material is very susceptible to Delayed Hydride Cracking (DHC), the residual stress in the tube resulting from the expansion of the tubes at the rolled joints has to be kept to a low value by a nominal interference fit between the outside diameter of the pressure tube and the inside diameter of the end-fitting. Such joints, known as zero-clearance rolled joints, have been developed for leak rate less than one cubic centimeter per year and pull out strength of more than 50,000 kg for 235 MWe PHWR pressure tubes.

### **Irradiation Behaviour of Zirconium Alloys**

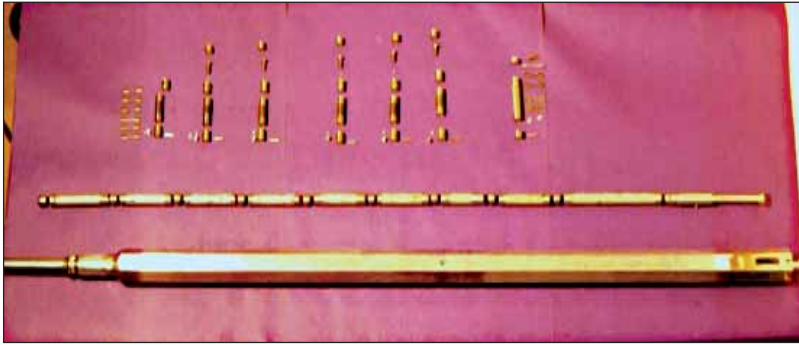
The most important effect of fast neutron exposure on the pressure tube is enhancement in its secondary creep rate. The fast neutron flux in the reactor alters the creep behavior of these alloys and at operating temperatures of PHWRs, radiation creep is seen to be larger than the thermal creep. So the radiation

creep rate of the two indigenously developed alloys of zirconium at the operating stresses and temperatures seen in the PHWRs needed to be determined. Irradiation of zirconium alloy specimens in FBTR offers advantage of attaining higher damage rates in a shorter time as compared to irradiation in PHWRs. This is due to the high flux and the harder neutron spectrum of FBTR. An irradiation experiment was designed and carried out in FBTR to determine the in-reactor creep behaviour of indigenously developed Zircaloy-2 and Zr-2.5%Nb alloy. As irradiation of full size pressure tube samples is not possible in FBTR due to the reactor core assembly geometry, miniature coolant tubes, which are geometrically similar to the full size pressure tubes, were produced for use in the experiment. The samples tested were in the form of pressurized capsules (PCs) made from these miniature coolant tubes with predetermined pressures to generate stresses in the tube walls that are similar to the stresses in the operating pressure tubes in PHWRs.

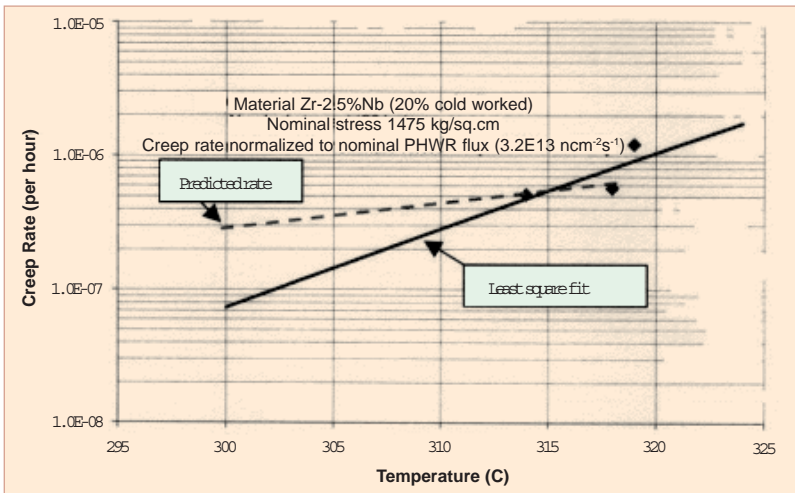
A total of 30 PCs were fitted into six special subassemblies, which were loaded in FBTR core simultaneously and were withdrawn one by one after a specified duration of irradiation.

After irradiation, the special sub-assemblies were transferred to the hot cells for post irradiation examination. Each special sub-assembly consists of one stainless steel Irradiation Experiment Capsule (IEC), which contains five PCs. The PCs were extracted from the special sub-assemblies remotely, taking great care to avoid any deformation or surface damage, as this would affect the accuracy of measurement of the diametral creep. Before carrying out the actual extraction, necessary devices and gadgets were fabricated, assembled and posted into the hot cells after detailed mock-up operations. Specially designed fixtures and dimension measuring device were used, in a specially erected workstation near the hot cells, to measure the diameter of the PCs accurately with minimum man-rem exposure.

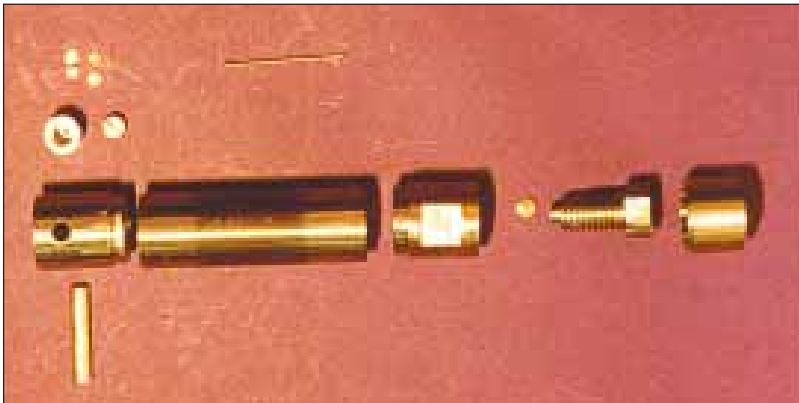
The measured creep data was normalized for thermal reactor flux conditions by taking the nominal fast flux ( $E > 1$  MeV) value in thermal reactor as  $3.2 \times 10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup>. The measured in-reactor creep rates for indigenous zircaloy-2 and Zr-2.5% Nb alloy are comparable to those reported in international open literature. These results gave confidence in assuring the performance of the indigenously developed alloys.



Pre-assembly view of special carrier subassembly, irradiation capsule and its contents



Temperature dependence of creep rate of cold worked Zr-2.5%Nb alloy under irradiation



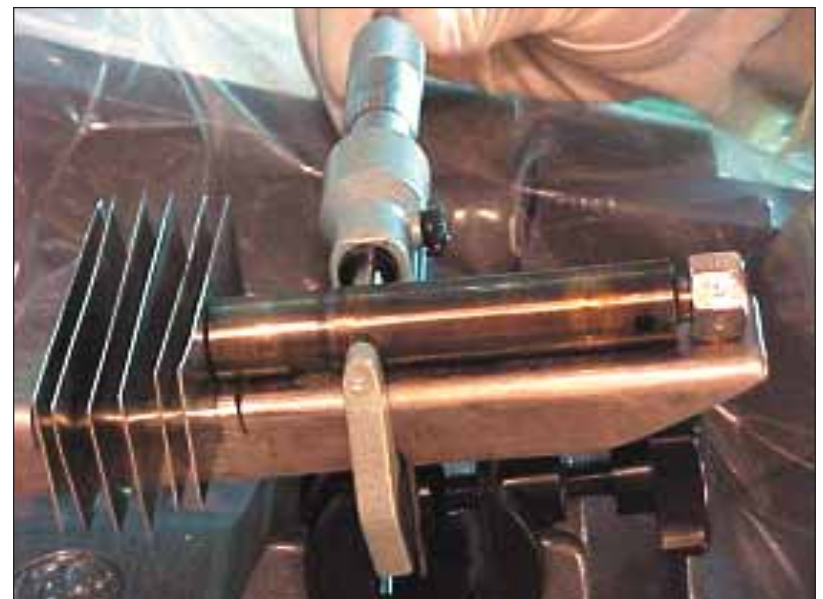
Close up view of pressurized capsule before assembly

### Development of Dry Channel Visual Inspection System

For the visual in-service inspection of the coolant channel of the PHWRs, it is necessary to have a device which can carry out a comprehensive scan of the entire bore of the coolant channel with good clarity and resolution and has reasonably accurate capability to size the objects being viewed. It should also be possible to remotely position the inspection device anywhere



Dismantling of irradiation capsule in hot cell



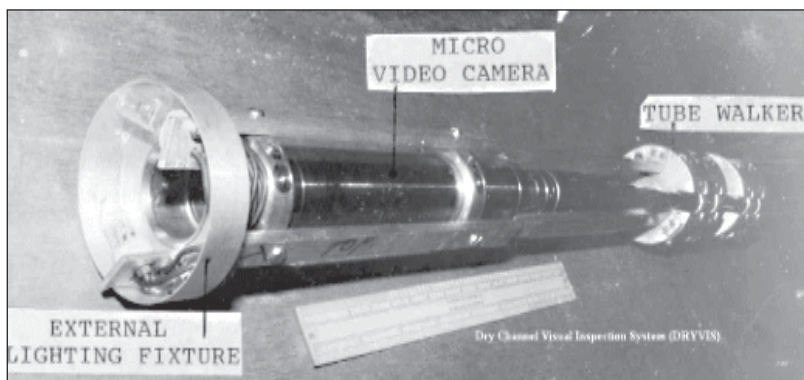
Post-irradiation measurement of diameter of pressurized capsule

within a given channel with low personnel radiation exposure.

To meet these requirements, a visual inspection system, called "DRY channel Visual Inspection System (DRYVIS)" was developed. The DRYVIS comprises of a tube walker, a radiation resistant micro video camera based CCTV system, an external illumination head and a grating for sizing of indications. The tube walker is a compact pneumatically actuated device, which is capable of being propelled within the bore of the tube with only trailing flexible pneumatic lines.

The DRYVIS has been successfully used to carry out internal video inspection of the pressure tubes K-07 (RAPS-2) and





*DRYVIS inspection system*

G-09 (RAPS-2) and calandria tubes O-11 (RAPS-2) and K-19 (NAPS-1)

### Sliver Sample Scraping Technique

For assessment of safe operating life of pressure tubes, it is necessary to estimate the hydrogen concentration in the pressure tube material and to establish hydrogen or deuterium pick up rate by the pressure tube under operating conditions by periodically estimating the total hydrogen concentration accumulated in it. To carry out such assessment without removal of pressure tube and to increase the availability of the reactor, it is necessary to obtain sliver samples of the pressure tube material without affecting the integrity and residual service life of the pressure tube.

The “Sliver Sample Scraping Technique”, which is remote controlled non-destructive technique, was developed to obtain samples from specified locations within the bore of pressure tubes of PHWRs

Dry sampling tool, known as Sliver Sample Scraping Tool (SSST) and wet sampling tool known as WET scraping Tool (WEST) were developed to obtain sliver samples from the pressure tubes in dry and water filled conditions respectively. In the process, a sliver sample of 0.1 mm thickness and 90 mg average weight is obtained in such a way that scraped region contour, created inside in the bore of the pressure tube, does not lead to loss of its integrity. This complex technology is now assimilated for large-scale deployment in Indian PHWRs.

WEST was used successfully at MAPS-1 reactor in August 2001 to obtain 15 samples from five channels and again in September 2002 to obtain 12 samples from four channels, at RAPS-1 reactor in October-November 2002 to obtain 261



*Dry scraping tool*



*Wet Scraping Tool*



*Multiple Scraped Region within PT*



*Oxide Sample*



*Metal Sample*

samples from 87 channels, at NAPS-2 reactor in April 2003 to obtain 36 samples from six channels, and at KAPS-1 reactor in September 2003 to obtain 54 samples from nine channels.

### Development of Analytical Tools for Assessing Residual Service Life

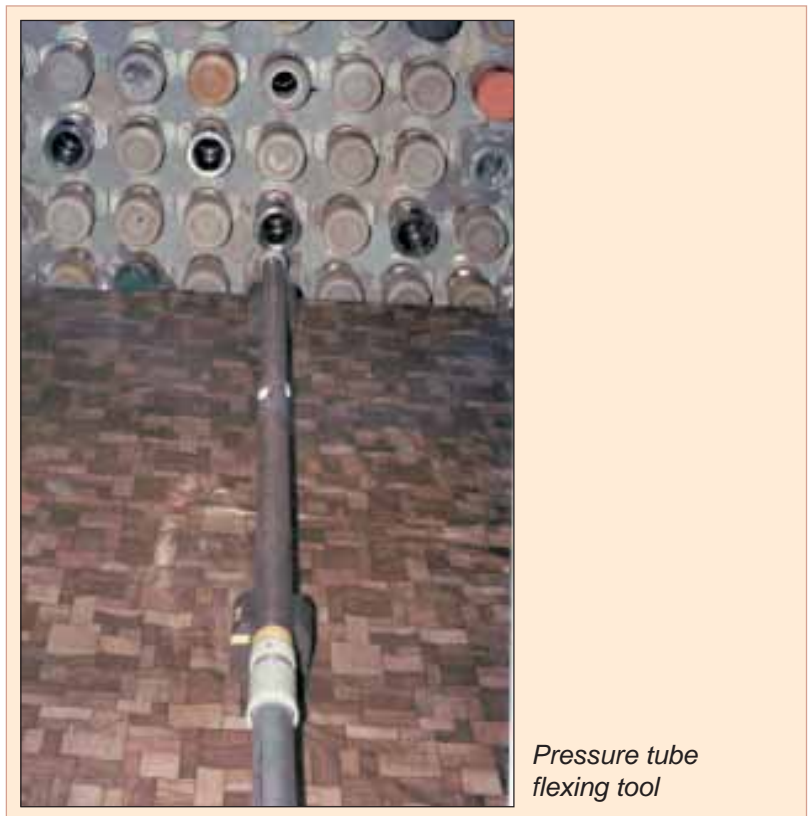
The pressure tube degradation mechanisms were modelled and incorporated into specially developed computer codes, such as: SCAPCA for radiation induced creep and growth (PT-CT

contact, sag of the channel, axial elongation and diametral creep are the manifestations of creep and growth). This code is used for estimation of pressure required for loosening of garter spring for ease of repositioning; HYCON for estimation of oxide thickness, hydrogen concentration and hydrogen pick-up rate at any axial position along the length of the pressure tube after any period of its in-reactor operation at varying power levels; BLIST for hydrogen diffusion, blister nucleation and growth; and CEAL for assessment of leak before break behaviour. These codes have been validated with respect to the results of in-service inspection and post irradiation examination. Development of analytical models has helped in evolution of more refined methodologies for assessing the safe residual life of coolant channel. Information gathered from various experiments simulating the degradation mechanisms, results of post-irradiation examination of the coolant channels and various research publications in international journals formed the bases for the above safety assessment methodologies. Today, the analytical models together with the safety evaluation methodologies have become important tools for assessing fitness for service of individual pressure tubes in different reactors.

### Life Extension of Coolant Channels

The loose fit garter springs of coolant channels assemblies, used in the first seven Indian PHWRs, are found to be susceptible to displacement from their initially installed locations due to vibrations caused by a number of construction and commissioning activities such as hot commissioning. This displacement could result in occurrence of premature PT-CT contact due to creep deformation of the both tubes in that channel, where such displacement of garter spring is significantly large. This may lead to formation of hydride blister over a period of reactor operation. The embrittlement and cracks caused by the hydrides may result in rupture and eventual failure of PT. There was a need to design and develop a remotely operable system which can precisely detect and relocate these displaced garter spring spacers in the coolant channel assemblies of new as well as operating reactor for extension of service life as a part of the programme for the life management of coolant channel of Indian PHWRs.

Pressure Tube Flexing Tool (PTFT) has been developed to reposition the displaced loose fit garter springs to create artificial



“Walking Mechanism” in new reactors (non-operating reactors). This technique uses the same phenomenon of the “Walking Mechanism” that is responsible for displacement of the garter spring during hot conditioning of the reactor, to reposition the garter springs in controlled manner. This technique was successfully employed in Narora-1 and 2 and Kakrapar-1 reactors.

To accomplish a similar task in an operating reactor, the Integrated Garter spring repositioning System (INGRES) was designed and developed for highly radioactive coolant channels. The INGRES system incorporates sophisticated electrical instrumentation and pneumatic, hydraulic and mechanical sub systems. The system is operated through a computer interface from a special control console outside the reactor building. The system was modified after each campaign and various versions have been built to improve the performance on the basis of experience gained.

The version INGRES-1S was used at MAPS-2 unit between June and August 1995. The version INGRES-2S was used at MAPS-1 in 1998 in five coolant channels and again in March-April, 2000 for repositioning garter springs in 31 coolant channels. The channel life was extended up to 9.5 Effective full power years (EFPYs).



The version INGRES-3S was used at MAPS-1 in 2002 in 29 channels to accomplish a total movement of 6676 mm of the garter springs and the channel life was extended up to 10.5 EFPYs.

The version INGRES-4S was used at RAPS-1 during 2002-2003 in 67 channels to accomplish a total movement of 34,160 mm of the garter springs and the channel life was extended up to 9 EFPYs.



*INGRES-3S tool*



*INGRES-4S tool*

### Development of Passive Catalytic Recombiner for Hydrogen Mitigation in Nuclear Power Plants

After the accident at Three Mile Island, USA, in the year 1979, mitigating the consequences of any released hydrogen under postulated accident scenarios in Nuclear Power Plants (NPPs) has been one of the objectives of nuclear safety related R & D all over the world. The importance of developing a hydrogen mitigation technology for IPHWRs was also recognised almost around the same time. The catalytic recombinations of hydrogen and oxygen have been proved to be the most attractive method for implementing a hydrogen mitigation strategy for the Indian NPPs. This is because of its effectiveness over a wide range of containment atmospheres in terms of temperature and presence of steam and the ability to promote homogenisation of the gas mixture due to buoyancy

induced gas flows. Towards developing this technology, several tasks such as (i) catalyst development and laboratory-scale performance testing, (ii) development of a box type recombiner device and (iii) performance evaluation tests for various catalyst samples in the engineering-scale test facility, HYMIS were successfully completed.

Various types of catalyst samples that were developed and tested so far are:

- a) Polyester fabric impregnated with Pt catalyst sandwiched between perforated aluminium plates
- b) Pt catalyst coated by chemical deposition on SS wire gauze
- c) Pd catalyst samples on alumina-coated SS wire gauze.
- d) Pt/Pd catalyst samples on SS wire gauze
- e) Pt and/or Pd based, powder compacted catalyst samples using either alumina or charcoal as carrier
- f) (Pt + Pd) thin film deposited by sputtering on SS plates

These were tested in the laboratory to determine, (i) effectiveness of the hydrogen-oxygen recombination reaction under dry and wet conditions, (ii) the effect of various contaminants such as  $I_2$ , CO,  $CO_2$ ,  $CH_4$  etc. on catalyst performance and (iii) mechanical integrity and aging effects.

For the purpose of engineering scale performance evaluation, a box type recombiner device was developed. Catalyst samples in the form of 'Catalyst Bearing Cards' were laid vertically in a parallel configuration at the bottom of the recombiner device. Due to catalytic recombination reaction, strong buoyancy induced convective flow is established over the catalyst surface. The metal housing of the recombiner is designed to promote natural convection flow through it with gas mixture entering and leaving through the openings provided at the bottom and top respectively. These performance evaluation tests were carried out in the HYMIS test facility in BARC. In most of the tests, the maximum attainable catalyst temperature was generally limited to around 573 K to 623 K and the achieved recombination time to bring the hydrogen concentration to 50 % of its original concentration was of the order of 25 to 30 minutes.

The research programme has thus led to successful development of Pt/Pd catalysts using various deposition techniques on different substrate materials and their

performance evaluation in laboratory-scale and engineering scale facilities. This work will help in evolving the hydrogen mitigation strategy for our nuclear power plants. The improvisation of the technology developed is likely to enhance the overall safety of Indian NPPs.

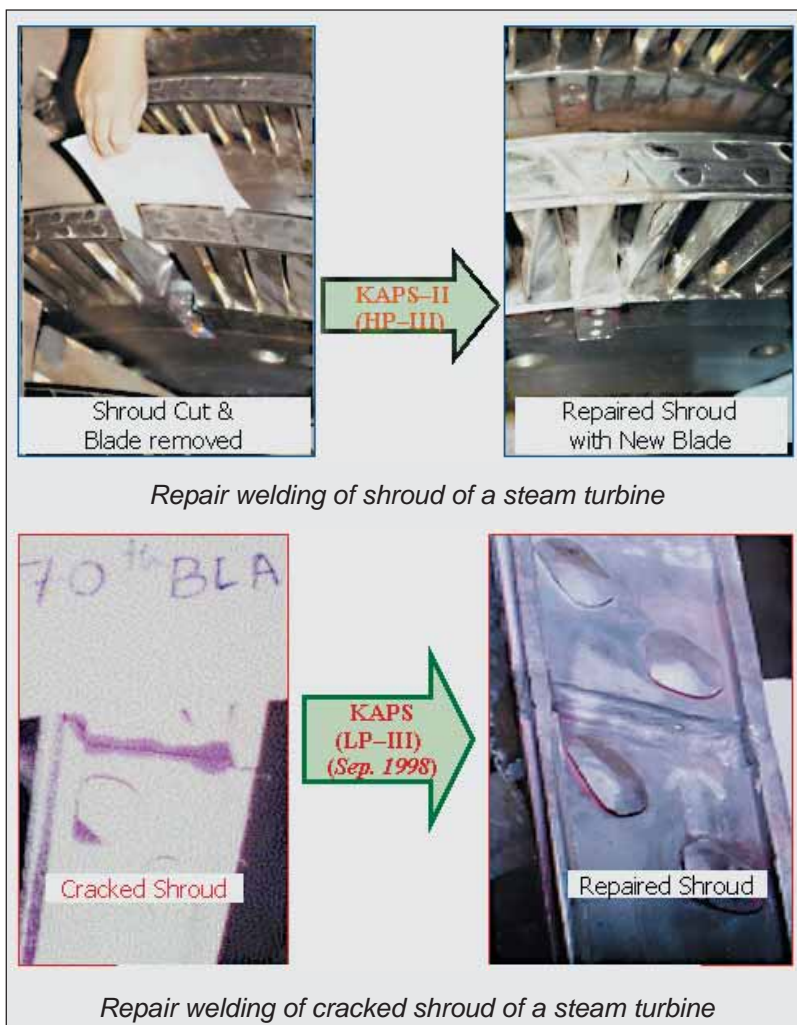
### In-Situ Repair Welding of Steam Turbines

In the high-pressure (HP) and low-pressure (LP) steam turbines of power plants, the blades and shrouds (used for packeting the blades) are prone to cracking/failure due to very high centrifugal and bending forces caused by resonance during operation. The conventional remedial approaches of total replacement of shrouds/blades or reduction in blade height and re-shrouding considerably increase the duration of turbine outage thereby reducing the performance and availability factor of the turbines. This necessitated in-house development of repair welding procedures for (a) shrouds of LP and HP turbines, (b) blades of LP turbines, and (c) build-up repair of

worn-out tenons in LP turbines. We innovated and successfully implemented the systematics for in-situ repair welding of such cracked blades/shrouds, including replacement of a root-cracked blade by shroud re-welding, in 6 steam turbines at 3 NPCIL power plants, viz. KAPS, NAPS and MAPS. One of the keys to the successful implementation of welding procedures was the localised post-weld heat treatment (PWHT) of repair-welded regions using a specially designed setup. All the repair-welded components are performing satisfactorily for up to five years now. These successful in-situ weld repairs have established a new technically and economically viable alternative to costly total replacement and prolonged outages due to repair downtime, thereby improving plant performance and availability factor.

### Indigenous Development of Fast Breeder Reactor Materials

Materials play a very crucial role for the successful development of fast reactor technology. Fast breeder reactor (FBR) components operate at high temperatures under complex loading and environmental conditions, which include sodium coolant, water and superheated steam and high fast neutron flux depending on the component. The FBR materials are broadly classified as core, structural and steam generator materials. Core components consist of the fuel pins and wrapper tubes which together form the fuel subassemblies. They have a limited design life of about two years. Core materials operate under intense neutron irradiation (flux  $\sim 10^{15}$  n/cm<sup>2</sup>) and are exposed to flowing sodium at temperatures up to 973 K. Austenitic stainless steels in 20% cold worked condition are generally used because they have good mechanical properties at high temperatures, and are compatible with liquid sodium and the ceramic fuels of uranium and plutonium. A consequence of the high flux of fast neutrons is the occurrence of very high levels of radiation damage in the core structural materials and this can be as large as 100-200 displacements per atom (dpa). This leads to excessive increase in the volume of fuel clad and wrapper tubes (void swelling) and limits the permissible residence time of the fuel subassemblies in the core and hence the achievable fuel burn-up. High burn-up is an important consideration in the economic viability of fast reactors as it reduces the fuel cycle cost.



Structural components operate at moderate temperatures up to 823 K and should be compatible with flowing sodium. These components are exposed to low levels of neutron irradiation and are designed for 40 years of operation. Mechanical properties such as creep and low cycle fatigue strength at these temperatures, corrosion resistance and weldability, are important considerations in the choice of materials for structural components. Heat generated through nuclear fission is extracted by liquid sodium and is converted into steam in the steam generator where hot sodium and water/steam are separated by thin walled tubes. Any leak in the tubes would lead to violent sodium-water reaction and affect other tubes in their vicinity. Therefore, austenitic stainless steels resistant to aqueous and caustic corrosion are selected. Ferritic steels are employed for steam generator components in view of their good mechanical properties and excellent resistance to stress corrosion cracking.

For PHWR most of the necessary material resources like zirconium were indigenously produced. For the FBRs too a similar philosophy was adopted. Considering that the steel industry in India is well established, efforts were made to interact and collaborate with the industry to develop the special steels to stringent specifications required for nuclear applications. While most of the core and structural materials used in the Fast Breeder Test Reactor (FBTR) were imported, a conscious decision was taken to ensure that all the materials required for PFBR would be produced within the country.

### Plates, Tubes and Forgings

Modified type 316 SS was chosen for FBTR as the fuel clad and wrapper material. It is now well recognized that swelling of these steels would be too high at displacement doses of 100-200 dpa and these steels would not be acceptable for the economic viability of commercial breeder reactors. By modifying the chemical composition, it was possible to increase very significantly the void swelling resistance of this grade of austenitic stainless steel. This modified grade, called alloy D9, was selected for PFBR core. Modifications in composition include increase in nickel content, lowering chromium content and adding controlled quantities of titanium and silicon to type 316 SS.

The indigenous development of alloy D9 started with a large number of laboratory melts at IGCAR, Kalpakkam, to optimize

the melting, casting, forging and heat treatment conditions. Based on the laboratory studies, commercial heats were made at MIDHANI, Hyderabad. Using these ingots, clad and wrapper tubes were successfully produced. The processing technology was fully developed to produce the estimated 50,000 fuel clad tubes of 2.7 metre long and 0.45 mm wall thickness required for PFBR. Whereas alloy D9 will be used for the initial core of PFBR, efforts are underway to develop modified grades of alloy D9 with higher silicon and phosphorus called D9I for clad tubes.

Structural components of FBTR have been made using nuclear grades of 304 and 316 SS. In order to reduce susceptibility of welds to corrosion and stress corrosion cracking, low carbon grades of 304 and 316 SS strengthened by nitrogen alloying called 304L(N) and 316L(N) SS, have been selected for PFBR. Another strategy was to eliminate the number of welds by using large size plates and long size tubes. 316L(N), 304L(N) SS and modified 9Cr-1Mo steel plates currently produced in the country are much smaller in dimensions required for PFBR, in thickness, length and width. However, it was realised that facilities do exist in SAIL steel plants that could be combined to produce these materials in the required dimensions. Materials were therefore melted in one plant and transported to another where these were rolled into plates. Development of these plates required augmentation of facilities for heat treatment and final finishing which did not

*“Ever since its inception, MIDHANI has been playing a stellar role over the last three decades through the supply of a wide spectrum of strategic metals and alloys for the Nuclear programme. Supplies to DAE have always been a challenging task for MIDHANI, considering the stringent material specifications to which the materials are commercially manufactured and evaluated. Several daunting problems have been faced during the course of development and manufacture. They have been summarily surmounted, with the help of in-depth analysis and use of advanced metallurgical techniques.”*

**– Devasis Chowdhury, CMD,  
Mishra Dhatu Nigam Ltd.,  
Ministry of Defence, Hyderabad**



exist at SAIL plants. Some industries in the private sector in the vicinity of integrated steel plants were also included for effective and economical production of these plates. As a result it is now possible to produce all plates in sizes required for 304L(N) SS, 316L(N) SS and modified 9Cr-1Mo steel within the country for the first time. Their evaluation has given very promising results compared to the imported materials.

Modified 9Cr-1Mo steel is selected for PFBR steam generators based on superior corrosion resistance and high temperature mechanical properties compared with 2.25Cr-1Mo used in FBTR. The seamless tubes of modified 9Cr-1Mo steel in the sizes required by PFBR (23 meters long) are not produced so far in the country. A collaborative programme was initiated between IGCAR, MIDHANI and NFC. Steel meeting stringent requirements was produced by electroslag refining process at MIDHANI and the forged rounds were then converted into long seamless tubes at NFC. Strict quality control was carried out at all stages including development of innovative non-destructive testing techniques.

Based on R&D efforts in IGCAR, optimum forming conditions were also identified and implemented in the industry to process various products like plates, tubes and forgings of various steels. This has generated full confidence that the PFBR materials can be produced within the country at a competitive cost.

### Development of Welding Consumables

The need to develop special grade welding consumables for PFBR arises from the specialised requirements for high temperature service and for conformity with specific design requirements that cannot be met by commercially available products. Experience gained during welding of FBTR components served as a guide in the selection of suitable welding consumables for PFBR with optimised chemical composition. For gas tungsten arc (GTA) and shielded metal arc (SMA) welding of 316L(N) SS components, ER16-8-2 (16%Cr-8%Ni-2%Mo) and modified E316-15 welding consumables, respectively, have been chosen in view of their good microstructural stability, creep strength and toughness. The ER16-8-2 filler wire has been indigenously developed through collaboration between DAE and MIDHANI. For the E316-15 welding electrodes, chemical composition was optimised through close control of carbon and nitrogen contents

*“Several Divisions of Godrej have had the privilege of working with various units of Department of Atomic Energy. The rich and varied experience in working with DAE has certainly enriched Godrej in many ways. Many new capabilities have also been added while executing DAE projects. Working with different metallurgists for welding and machining, precision manufacturing of complex parts, uncompromising and exacting quality measurements of components and assemblies and the performance tests to finally have certified reliability of the end product, have all led to development of critical capabilities to satisfy these requirements. The exacting and uncompromising requirements that are the hallmark of DAE projects have also spurred our business to improve quality. Overall, working with DAE has led to development of improved processes and extending our capability envelope. This enables our business to deal with other customers having similar requirements, worldwide.”*

**- J.N. Godrej,**  
CMD, Godrej & Boyce Mfg. Co. Ltd.,  
Mumbai.

to ensure improved microstructural stability and creep strength. The ferrite content in the weld metal was also optimised to ensure adequate hot cracking resistance during welding and to restrict the occurrence of embrittling phases during high temperature service. As slag detachability becomes a problem with basic fluxes that confer high weld metal toughness, the major challenge during indigenous development of these basic-coated E316 welding electrodes was to simultaneously achieve the desired ferrite content, good slag detachability and high toughness. Successful indigenisation of this welding electrode, in collaboration with electrode manufacturers, has been possible by carefully adjusting the flux-coating composition based on R&D inputs provided to the manufacturers.

For welding of modified 9Cr-1Mo steel, suitable filler wires for GTA welding have been indigenously developed in collaboration with MIDHANI. The required toughness in the SMA welds after post weld heat treatment (PWHT) was achieved by imparting minor modifications in the nickel, manganese, niobium, vanadium and nitrogen contents of the steel. It has



*“Our company was fortunate to have a close association with IGCAR for development of welding electrodes for welding of modified 316 materials and modified 9 Cr- (P91) materials. Though imported consumables were available for usage and could have been imported, only the persistent efforts and encouragements of the IGCAR team enthused manufacturers like us to take on the challenge and work towards development of indigenous welding electrodes. A number of discussions were held (with IGCAR team) and I am pleased to go on record that they were extremely useful and result oriented. Apart from this, we had the benefit of your personnel using your sophisticated equipments to determine critical material properties to ascertain the quality of our products. So we had the benefit both men and machines throughout the development. I am confident that the future years will see much more co-operative efforts between DAE and industry.”*

**- N.Sivagurunathan,**  
*Managing Director, Mailam India Limited.*

## **Mechanical Properties of Fast Reactor Materials**

High temperature operating requirements for core, piping and steam generator components have drastically increased with the decision of designing PFBR for 40 years of life. The components in PFBR operate for extended periods of time at temperatures between 0.3 to 0.5 of their absolute melting point and have design lives that are limited by creep. Service conditions experienced by components would also involve cyclic loading during start-up and shut down or during power transients leading to fatigue. The fatigue failure resulting from start-ups and shut-downs occurs under essentially strain controlled conditions, since the surface region is constrained by the bulk of the component. The combination of cyclic loading and steady state operation of the reactor at elevated temperatures introduces a special phenomenon known as creep-fatigue interaction damage that can have a detrimental effect on the performance of components. When temperatures are high enough, time-dependent creep strains as well as cyclic (fatigue) strains can be present and interpretation of the effect that one has on the other becomes extremely important. For example, it has been found that creep strains can seriously reduce fatigue life and/ or that fatigue strains can seriously reduce creep life. It is the quantification of these effects and the application of this information in the development of design curves and life prediction procedures has been the primary objective of research on mechanical properties evaluation at IGCAR.

Modified grade type 316 SS, with strict control on chemical composition, inclusion content and grain size, different from the standard grade of this alloy, has been used for fabrication of high temperature structural components of FBTR at Kalpakkam. Most of these components have a design life of 30 years. Systematic investigations on the long-term creep behaviour of this material for durations up to 16 years were conducted. These studies clearly brought out the micromechanisms of creep deformation and fracture in this alloy and paved the way for carrying out reliable extrapolation to service conditions. Detailed assessment of creep properties of 316 SS has revealed that there are significant heat-to-heat variations in the creep properties which were correlated with variations in chemical composition of minor elements such as carbon, nitrogen and boron as well as variations in grain size, although these variations were within the range of material



*Modified electrode-coating unit at IGCAR*

been possible to meet the required minimum toughness in indigenous welding electrode, developed in collaboration with electrode manufacturers, by using alloyed core wire and carefully controlling the flux-coating formulation.

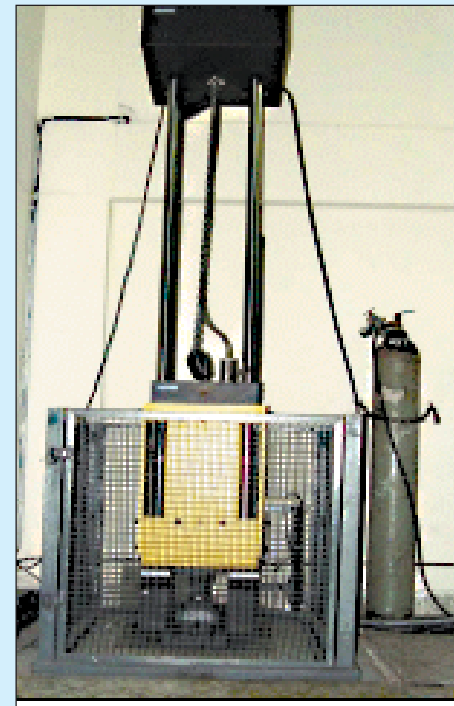
specifications. These studies contributed to arriving at the specifications for low carbon, nitrogen alloyed 316 SS, designated as 316L(N) SS, for the prototype fast breeder reactor (PFBR).

### Development of Testing Methodology for Evaluation of Fracture Toughness

Drop-weight and Charpy-V notch tests are widely used in nuclear power industries to determine the reference nil ductility transition temperature ( $RT_{NDT}$ ) of the materials susceptible to ductile-brittle transition. However, the appropriate design parameter against brittle fracture is dynamic fracture toughness,  $K_{Ic}$ . A novel technique for determining  $K_{Ic}$  from drop-weight tests was developed by analysing load-time traces obtained from the attached instrumentation system. The method was applied to determine  $K_{Ic}$  for base materials and welds and even extended to the heat affected zone of 9Cr-1Mo steel with multiple microstructural regions. In the ductile fracture regime, test methods have been developed for the elastic-plastic fracture toughness parameter  $J_{Ic}$ , along with the conventional use of Charpy machine for determining fracture energy, to obtain fracture behaviour at the actual operating temperatures. These studies have helped to ensure that fracture properties do not degrade due to ageing effects at the temperature of operation.



*Instrumented Charpy impact testing machine*



*Instrumented drop-weight testing machine*

### Advances in Metal Forming

The demanding and hostile environment in the PFBR necessitates that the components from special materials are processed by judicious selection of hot, warm or cold forming methods. To achieve the required service properties, it is essential that the microstructural development during hot working should be carefully controlled and defects and flow instabilities are avoided. The optimum processing parameters namely, temperature, strain rate and reduction ratio, currently followed in industry are based on extensive trial and error techniques that are costly and time consuming. Therefore, new methodologies are required that use constitutive flow behaviour of the material to adequately characterise the regimes of temperature and strain rate relevant to hot working. Towards this goal, deformation behaviour of various materials of interest to fast reactor programme employing compression tests over a wide range of temperatures and strain rates. The “safe” processing windows delineated by dynamic recrystallisation (DRX) and dynamic recovery (DRY) are identified. In certain regimes of temperature and strain rate, austenitic stainless steels exhibited flow localisation and these “unsafe” domains need to be avoided during mechanical working. The usefulness of these maps for controlling industrial processes such as press forging, extrusion and hammer forging was validated under industrial process conditions.

*The deduction of optimum process parameters and their implementation at Nuclear Fuel Complex (NFC), Hyderabad has resulted in lower rejection rates (less than 2 %) and higher yields in the production of nuclear grade stainless steel tubes by extrusion. A new methodology to refine the safe processing window for better control of microstructure and mechanical properties was also identified based on the principles of DMM and activation energy.*

The finite element modeling (FEM) of hot-working (extrusion) and cold-working processes (petal forming and nozzle pullout) is very useful in understanding the variation of process parameters in the deformation zone. The objective of simulation in hot working is to process the material without any undesirable metallurgical defects, whereas in cold working, the design of tooling to produce near net shape components is the aim. The strains, strain rates and temperature in the deformation zone were obtained for various ram speeds using FEM. This local variation of the operating parameters viz. strain rate and temperature were then compared with the “safe” and “unsafe” domains of the processing maps for arriving at the optimum parameters for hot extrusion of alloy D9 and 304L stainless steels.

### Manufacture of Seamless Stainless Tubing and Related Equipment

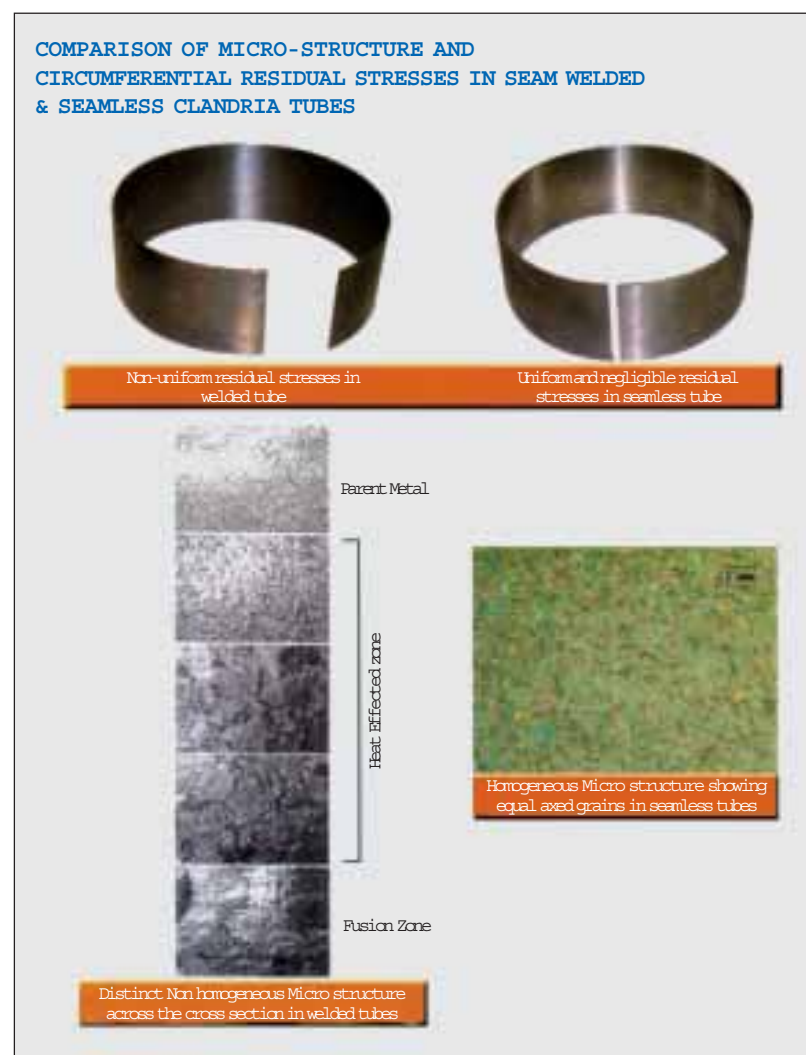
Production of seamless tubes for special applications is one of the important production activities. For this purpose a facility of hot extrusion press and cold pilger mills with related finishing and inspection equipments for manufacturing quality seamless tubes of zirconium alloy for, application in nuclear power reactors was set up in the early 70's. It is known that demand for seamless tubes in a developing economy gradually increases till it reaches around 30-to 40 % of the total requirement of tubes and pipes. Confidence gained by development of manufacturing technology for production of zircaloy seamless tubes for nuclear application resulted in harnessing spin-off technology for production of seamless tubes in materials generally difficult to hot roll (in other than extrusion process). NFC, therefore augmented its seamless tube manufacturing facility by adding a vertical piercing press, series of induction

furnace and large size pilger mills to meet existing demand of power sector, engineering, fertilizer and electrochemical industries.

Manufacturing technology was developed for production of seamless tubes in materials hitherto imported by the domestic industry for specialised applications in aeronautical, engineering and nuclear field. Extrusion of tubes and profiles in materials like cupro-nickel, titanium alloys, niobium alloys, silver, Inconel, bimetallic materials and other special alloys has generated

*NFC has successfully produced large quantities of 316 Ti stainless steel tubes for the Navy and 321 SS tubes for light combat aircraft.*

confidence both in the process and technology development. NFC has successfully developed and produced large quantities of 316 Ti grade stainless steel tubes for the Indian Navy, 321





SS tubes for Light Combat Aircraft, modified 9Cr-1Mo steel tubes for power generation industry, and 316 SS clad tubes for FBTR at Kalpakkam. NFC has emerged as a technological centre for developing manufacturing process for production of high quality seamless tubes of stainless steel and other special alloy materials.

### **Sensitization Studies of Nuclear Grade AISI 304, 316, 316L(N) SS and their Weld Metals**

Austenitic stainless steels are prone to sensitisation due to intergranular precipitation of chromium-rich carbides and the concomitant depletion of chromium in the regions adjacent to the grain boundaries. This occurs generally during prolonged exposure or continuous cooling of these steels in the temperature range 723 – 1123K. In the sensitized condition, the steels are susceptible to intergranular corrosion and intergranular stress corrosion cracking in corrosive environments resulting in premature failure of fabricated components. In order to prevent failures arising out of sensitization in welded components, detailed investigations were conducted on nuclear grade AISI 304, 316 and 316L(N) SS (imported as well as indigenously developed) and its weld metal prepared using indigenously developed modified 316 (N) electrodes. Time-temperature-sensitization (TTS) diagrams were established using ASTM A262 standard practice E for various degrees of prior cold work. A mathematical method was developed to calculate critical cooling rate (CCR) above which there is no risk of sensitization from the isothermal sensitization data. Continuous cooling sensitisation diagrams derived from the TTS were found useful to arrive at optimum parameters (heating rate, soaking duration and cooling rate) to be followed during various stages in the manufacture of welded components.

### **Life Prediction of PFBR Materials by Artificial Neural Network Approach**

LCF and creep-fatigue interaction data generated in house on 316L(N) stainless steel was used to assess the capability of Artificial Neural Network (ANN) approach for life prediction. LCF and creep-fatigue life prediction carried out by ANN approach gave values very close to the actual lives. These investigations revealed that the success and accuracy of prediction depends upon (i) quality of data, (ii) extent of coverage of training data

in the domain of prediction, (iii) selection of appropriate input variables, (iv) transformation of input variables and (v) optimization of neural network parameters. In order to design PFBR for 40 years of lifetime with a load factor of 75%, detailed investigations were performed to obtain creep allowable stresses for Mod. 9Cr-1Mo steel at a life of 2,63,000 h. Allowable stress values predicted by Larsen-Miller parametric approach and multilayer perception ANN lie very close to those obtained by extrapolating RCC-MR (French Code) data at a creep rupture life value of 2,63,000 h. These investigations gave the confidence that LMP and ANN can be used as complimentary techniques for extrapolating creep rupture lives for service conditions of PFBR steam generator.

### **Weldability of Austenitic Stainless Steels and Ferritic Steels**

Weldability studies focus on ensuring that components are welded without defects and that the welded components possess adequate mechanical and other engineering properties to perform satisfactorily during their design life. Detailed weldability evaluation of PFBR materials was carried out to obtain clear quantitative guidelines for excluding the possibility of hot cracking in stainless steels while at the same time avoiding excessive conservatism. Weld metal and heat affected zone (HAZ) cracking propensity, quantified in terms of the brittleness temperature range (BTR), was studied in Alloy D9 and 316L(N) stainless steel. The D9 alloy, despite having low P+S (0.014 wt-%), showed high susceptibility to solidification and HAZ cracking because of the fully austenitic microstructure and segregation of Ti, S, N and C to the grain boundaries. The study showed that a Ti/C of about 4 showed least susceptibility to solidification as well as HAZ cracking and highlighted the importance of controlling weld metal N to minimise cracking. Studies on effect of N on cracking in 316L(N) base metal and modified 316 weld metals showed that N has no detrimental effect on cracking, if  $Cr_{eq}/Ni_{eq}$  is maintained to obtain a ferritic solidification mode (FA) during welding. Weld metal cracking in IN 718 superalloy could be minimised by using lower heat input and by using alloy 82 filler metal rather than consumable of matching composition.

The major technological issues in weldability of modified 9Cr-1Mo (grade 91) steel are determination of critical preheat temperature to avoid hydrogen assisted cracking (HAC) and

achievement of adequate toughness in the weld metal. Weldability studies on grade 91 revealed that susceptibility to HAC is a strong function of composition. Baking of electrodes and control of preheat temperature were found to be critical steps in the control of HAC. Achieving good toughness in the weld metal produced by processes that involve fluxes (like SMAW, SAW and FCAW) in grade 91 steel is a challenging task due to the higher inclusion content compared to fluxless welding such as GTAW. To improve weld metal toughness, the chemical composition of welding electrodes was optimised by controlled additions of Ni, Mn, Nb and Si and by avoiding delta-ferrite in the deposited weld metal.

### **Mechanical Properties of Welds and Weldments for Component Design**

High temperature nuclear design codes did not contain adequate design data for welds; instead design has been largely based on properties of the base metal. In the absence of sufficient guidelines in the codes, extensive studies on the creep behaviour of modified 316 SS and 316L(N) SS weld metals and weldments were performed. It was noticed that creep strength of the weld metal is significantly lower than that of the base metal. The delta-ferrite in the as-welded 316 SS, which is essential for avoiding hot cracking during welding, undergoes transformation to brittle intermetallic phases during creep, thereby lowering weld metal creep strength and ductility. These studies enabled arriving at appropriate creep strength reduction factors for welds at different temperatures for realistic design of components.

Extensive analysis on creep deformation and fracture was conducted on base, weld, weldments and simulated HAZ structures of 2.25Cr-1Mo, 9Cr-1Mo and Mod. 9Cr-1Mo steels with a view to optimizing performance of the weldments. These investigations identified that the width of intercritical zone and coarse grain regions of HAZ have to be controlled to improve performance of ferritic steel weldments. It has been established that the optimization of welding conditions is necessary to maximize the amount of fine grain bainite/martensite in HAZ.

### **Welding of Dissimilar Metals**

Welding of dissimilar-metals becomes a necessity, as different materials have to be chosen for different components

operating under different service conditions. Differences in physical and mechanical properties of base metals and their influence on the in-service behaviour of the weld joints as also alloying between the base metals and filler metal are major considerations. In the steam generator circuit of PFBR, 316L(N) SS pipes from the intermediate heat exchangers have to be welded to the modified 9Cr-1Mo steel pipes of the steam generators. These dissimilar metal welds are prone to large-scale premature service failures, leading to expensive plant outages, due to the difference in thermal expansion coefficients between the ferritic steel base metal and weld metal. The problem was circumvented by engineering a gradient in the thermal expansion coefficients along the joint by using an Alloy 800 transition piece. For welding 316L(N) SS to Alloy 800 and Alloy 800 to modified 9Cr-1Mo steel, ER16-8-2 and Inconel 82/182 welding consumables, respectively, have been chosen. Thermal cycling performance tests have shown that this tri-metallic transition joint has at least four times superior service life than the joints presently in use.

## **SURFACE MODIFICATION TECHNOLOGY**

### **Hard-Facing Coatings of PFBR Components**

All components in static/dynamic surface contact in liquid sodium are prone to adhesive wear (self-welding) or fretting wear because of the leaching of protective oxide layers by sodium. Hence, suitable hardface coatings on the contact areas are necessary for imparting adequate high-temperature in-sodium wear resistance. Cobalt-base alloys under the designation ERCoCr-A, B and C as per AWS A5.21 (Stellites) are the most commonly used hardfacing materials in nuclear reactors, and have been used in the FBTR as well. However, for in-core components, where radiation dose is very high, activation products, primarily  $\text{Co}^{60}$ , formed in cobalt-base alloys result in additional activity in the primary circuit. Such induced radioactivity during maintenance, component handling and decommissioning must be minimised. Hence, based on detailed induced radioactivity and shielding calculations, nickel-base cobalt-free ERNiCr-B has been chosen to replace cobalt-base alloys as the hardfacing material for all nuclear steam supply system components of PFBR made of 316L(N) and 304L(N) SS. Although ERNiCr-B hardface coatings were used



satisfactorily in fast breeder reactors, there are at least a few reports of failures in some hardfaced components operating at 823€K. Hence, to address this concern regarding reduction in hot-hardness of ERNiCr-B above 723€K, hardness degradation in long-term aged deposits was characterised. Based on time-temperature correlation, the estimated hot-hardness after exposure at 823€K showed that these hardface deposits would retain adequate hardness even after 40 years of service.

For hardfacing of PFBR components with ERNiCr-B, deposition procedures using the plasma transferred-arc welding (PTAW) process have been developed in collaboration with industry. The PTAW deposition procedures minimises dilution of the coating by the austenitic SS substrate thereby ensuring adequate hardness in the hardface coating. These PTAW deposition procedures have been successfully implemented for hardfacing (with ERNiCr-B) of some critical PFBR components, such as the roller bearings of the transfer arm and most significantly on the inner surface of grid plate sleeves at a location 450 mm away from the ends.

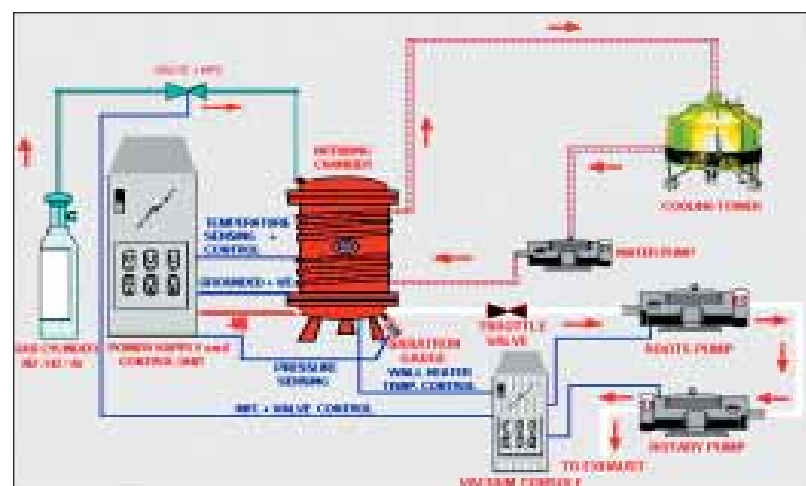
High-temperature wear-resistant bushes of ERNiCr-B are required in various components for in-sodium service in PFBR. These bushes, conventionally manufactured by precision casting, are not available in India and have to be imported at very high cost. As an import substitution measure, these bushes were fabricated using a novel procedure involving GTA deposition of ERNiCr-B on austenitic SS rods followed by precision machining of the hardface deposits. These bushes were found to meet the dimensional tolerance and surface-finish requirements and have excellent dimensional stability on high-temperature ageing. This procedure was successfully implemented for fabricating ERNiCr-B bushes for the transfer arm gripper assembly.

For minimizing fretting wear of tube bundle support structures

under flow-induced vibrations of steam generator tubes, aluminized Inconel 718 was chosen based on international experience. Either pack cementation process or vapour-phase aluminizing process, both of which require special equipment and proprietary procedures and reagents, have been used to produce aluminide coatings on Inconel 718 strips in different FBRs. A highly cost-effective and efficient process technology was indigenously developed and implemented for aluminizing of Inconel 718 steam generator tube-bundle support structures of PFBR, which eliminates exposure to corrosive halide activators associated with the cementation process. This technology uses a procedure involving thermal spraying of aluminium followed by diffusion heat treatment in vacuum to obtain the desired coating.

### Pulsed Plasma Nitriding Technology for Hardfacing

Although hardfacing using cobalt, nickel or iron base alloys has been used extensively in many fast reactor programmes,



Flow chart (a) and industrial level nitriding set up developed at IGCAR (b). This set up can carry out the pulsed plasma nitriding on chrome-plated stainless steel PFBR grid plate sleeves. This has been used to demonstrate that the PFBR grid plate sleeves can be nitrided and the product-  $Cr_2N$  coating meets the specifications for the final use in PFBR.



chromium nitride ( $\text{Cr}_2\text{N}$ ) coatings that are in use in Russian fast reactors are the best due to absence of induced radioactivity, high resistance to galling, fretting, and absence of decommissioning problems. The required properties of the coatings are (1) high surface hardness (~900 HV); (2) thickness to be ~60 – 80 mm (3) gradual variation in the hardness profile and (4) compatibility at high temperature with liquid sodium. Technical assessment of available techniques favours pulsed plasma nitriding process.

The process involves two steps, (1) Chrome plating of stainless steel component followed by (2) pulsed plasma nitriding of the desired locations in a vacuum chamber. Selection and optimisation of process parameters was based on several trial runs. The equipment for Pulsed plasma nitriding was indigenously developed.

### Commercialization of Industrial Plasma and Ion Implantation Technologies

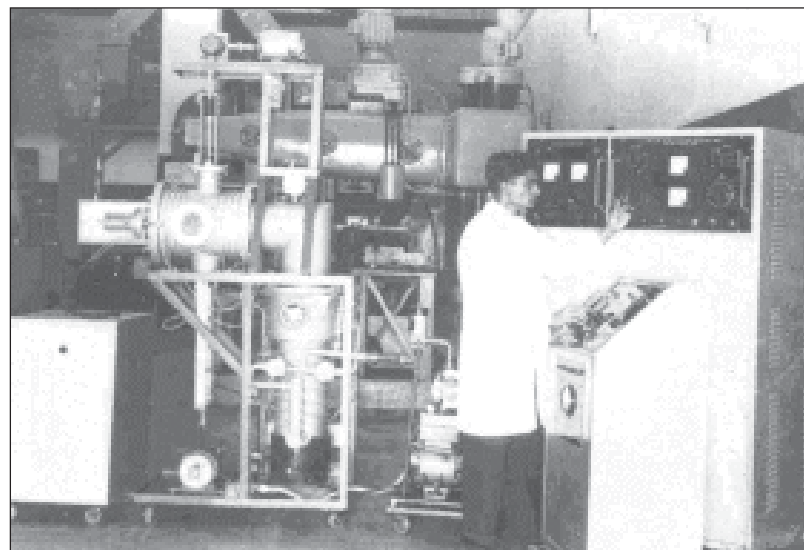
The plasma medium can be a versatile enabling tool in generating applications relevant to material, manufacturing, environmental and strategic sectors. An initiative taken by Institute for Plasma Research (IPR), Ahmedabad in 1990 to link the institute with industry and exploit its knowledgebase commercially has developed into the Facilitation Centre for Industrial Plasma Technologies. With a multi-disciplinary staff, the centre focused on technology development, demonstration, and commercialization.

### Electron Beam Equipment for Thermal Applications

Electron beam (EB) equipment development in BARC is about four decades old. The electron gun has evolved over the years and the designs have been standardised.

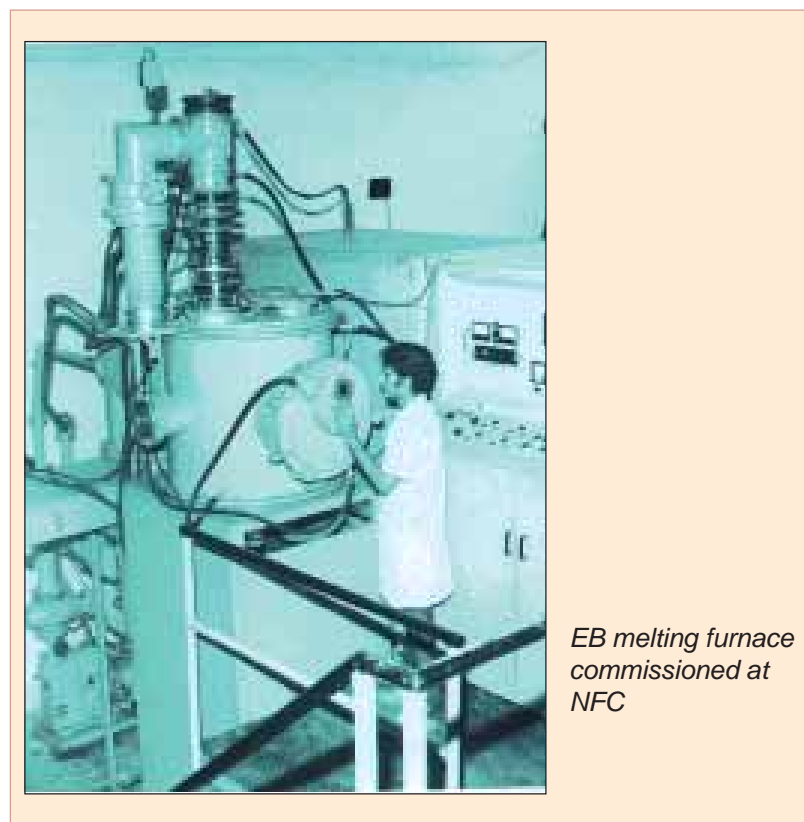
### Development of EB Melting Furnace

During the early sixties there was a requirement for the development of special materials like niobium and tantalum. These materials of high purity had application in nuclear component fabrication and this is when the design of a 5 kW Electron Beam Melting Furnace was initiated. The first unit to be developed was a 15 kV, 5 kW EB Melting unit in 1963. This unit was used for melting and purification of tantalum and



*The first electron beam melting furnace developed in BARC (1963)*

columbium. In 1969, an Electron beam-melting furnace of 15 kW capacity was developed..This was used extensively for over two decades for melting and purification of tantalum used in the manufacture of electrolytic capacitors. Subsequently, a memorandum of understanding was signed with a commercial manufacturing firm for development of such units indigenously, to fulfil the demands of other research laboratories.



*EB melting furnace commissioned at NFC*

## Development of EB Welding Machine

In 1967, the first prototype EB Welding machine was developed, mainly for the purpose of technology demonstration with the gun design capacity of 6 kW. This system was used to weld various metals and alloys like, titanium and its alloys, zircaloy-2, SS304 and aluminium. This unit was later used for welding of kovar eyelets for an image converter tube that was being indigenously developed and for welding of artificial heart valve samples.



*First EB welding machine at BARC (1967)*



*V V Ratnam explaining Electron Beam Welding to Dr. Vikram Sarabhai and Dr. A S Rao in 1971, G C Agarwal is also seen*

## Development of Partial Vacuum EB Welding Machine

In 1975, a project was sanctioned by the Aeronautics Research and Development Board, Department of Space, Government of India, to BARC, for indigenous development of

EB Welding Machines. The machine specifications were so chosen as to make it a versatile, general-purpose machine, which could be used by a wide spectrum of industries and institutions for batch production. The main objective of this development work was to keep down the imported content to less than 10%, cost-wise. As a result of this project an indigenous EBW machine including all the major sub-systems was developed for the first time with a capacity of 6 kW, at 150 kV DC. After commissioning, a number of metals samples, both similar and dissimilar were welded and weld qualification tests were done. Some of the dissimilar metals welded were (a) copper-to-SS, (b) copper-to-mild steel, (c) SS-to-mild steel, (d) SS-to-nickel, (e) aluminium-to-nickel, (f) SS-to-silver, (g) copper-to-nickel, (h) SS-to-zircaloy and many more. For example, in a copper-to-SS combination, thicknesses as small as 0.5 mm were joined together.

Several special welding jobs were carried out with this machine. Special mention must be made of canned motors for the

### *Examples of dissimilar metal welding done by the EBW machine*



*Copper-to-stainless steel*



*Stainless steel-to-sintered porous nickel*

Heavy Water Project, steel reflector boxes for Kamini Reactor and special steel coronets for the Ministry of Defense. With the experience gained in building this machine, a commercial model was built for the Machine Tool Prototype Factory, Ministry of Defense, with the help of local industry and commissioned at Ambarnath, near Mumbai, in 1992. This machine has been mainly used for welding of special materials for strategic applications.

### **Development of Portable Local Vacuum EB Welding Machine**

In 1975, a 40 kV, 10 kW partial vacuum, portable gun, EBW machine that could perform circular welds of diameters varying from 100 mm to 140 mm was developed. In this machine the job is kept stationary and the gun is rotated. Thus, a number of local welds on a large sized job, could be carried out by physically shifting the welding head to the next joint location and locally evacuating the volume near the joint.

### **Development of High Vacuum EB Welding Machine**

In 1999, a 80 kV, 24 kW EB welding machine was developed to weld thick sections of copper and its alloys. It was installed at Centre for design and manufacture, BARC.

### **Development of EB Evaporation Units**

The R&D efforts on EB evaporation work at BARC started around the year 1990, when an electron gun of cylindrical geometry rated at 30 kV with a capacity of 30 kW was developed for hard coating applications. Subsequently, smaller unit e-guns of the transverse type, were designed for optical coatings of laser mirrors and lenses. The unit has been used for producing various binary and ternary hard coatings for industrial applications.

A 200 kW, 60 kV evaporation unit that can produce a curtain type vapour stream for coating of strip, 200 mm to 500 mm wide was developed. The E-beam in the form of a strip about 100 mm long and 5 mm wide was bent by 270° and made to fall on a water cooled crucible that houses the charge. Various characteristics of this high-powered gun and the vapour stream were studied.



*200 kW EB evaporation system*

## **MODERATOR AND COOLANT SYSTEMS**

### **Heavy Water Board's Odyssey of Excellence**

Apart from the core and structural materials, the moderator and coolant are also important materials in a thermal reactor. Since PHWRs use natural uranium as fuel, fission neutrons have to be slowed down to increase the probability of subsequent fission events. This is done by heavy water in PHWRs. Since the first phase of the nuclear power programme envisaged a large number of natural uranium fuelled reactors with heavy water as the moderator and coolant, efforts have been placed in developing the heavy water technology and setting up strategic industrial scale plants for production of this vital material with great emphasis on self sufficiency.

Indigenous development of  $H_2S-H_2O$  exchange process for production of heavy water was taken up in early 1960 when a pilot plant was set up by the "Heavy Water and stable Isotope production section" of the then Atomic Energy Establishment, Trombay (AEET). This was followed by setting up a test loop for studying behaviour of various materials of construction under the operating conditions of this process. Initial work on this process generated important process and corrosion data and also provided valuable experience in generating and handling the highly toxic  $H_2S$  gas. Preliminary design of a hydrogen sulphide based plant was done during this period by a core group of young engineers of different disciplines. A plant based on electrolysis of water and hydrogen distillation was set up at Nangal in 1962.



With the increased demand for heavy water production, “Heavy Water Projects” had started functioning from 1969 as an independent unit of the Department with a mandate to build and operate Heavy Water Plants. The first commercial unit commenced production of heavy water based on the H<sub>2</sub>S-H<sub>2</sub>O exchange process at Rawatbhata, Rajasthan with a design capacity of 100 MT/Yr. Advantage was taken of the in-built extra steam generation capacity available in the reactors at RAPP to meet the process steam requirement of the Heavy Water Plant. The experience gained at Kota was effectively utilised in building the higher capacity plant at Manuguru, the first fully independent Heavy Water Plant in India.

Setting up of the first ammonia based heavy water plant at Baroda with foreign collaboration involved many challenges because of the very large sizes of the equipment designed for operation at 650 atmospheres of pressure at low temperatures. Transporting and crating an exchange tower weighing 530 MT as a single piece was a major challenge, which was also met successfully by Indian industry.

Experience gained in the construction and commissioning of the Baroda plant went a long way in the smooth implementation of the project at Tuticorin, which is based on a similar process but operates at a lower pressure. The plants at Thal and Hazira were set up entirely by indigenous efforts and were brought to stable operation within a record time.

The Heavy Water Plants bear testimony to the ingenuity of Indian engineers and industry and their capability to meet technological challenges. The strong stimulus for indigenisation enabled fruitful interaction with the industries in developing H<sub>2</sub>S gas boosters, canned motor pumps, special no leak double disc gate valves, with highly efficient ejector nozzles trays, sieve trays etc.

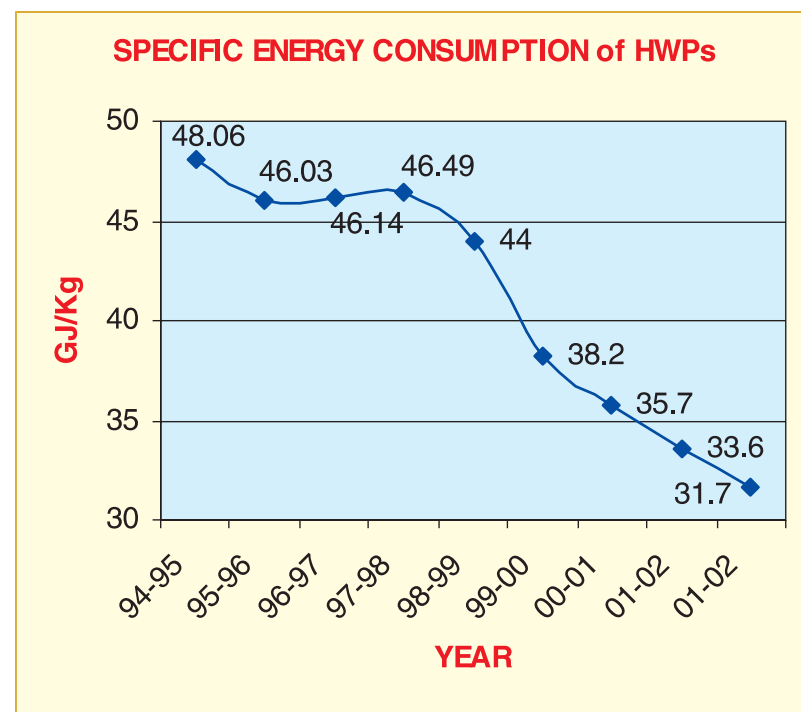
Heavy water produced in India was internationally accepted and we could export this heavy water to several countries including China and Korea. India is the only country in the world to have mastered two different technologies for production of heavy water, namely hydrogen sulphide water exchange process and ammonia-hydrogen exchange process.

### Improvements in the Process

Heavy water is Deuterium oxide – Deuterium being an isotope of hydrogen. Due to its nuclear properties heavy water

is used as moderator as well as coolant in the Pressurised Heavy Water Reactors.(PHWRs). A typical 220 MWe reactor requires about 275 tonnes of heavy water as the initial charge, which remains in the system. Heavy water is present in natural water in ppm levels (about 144 ppm) and due to its isotopic nature it is extremely difficult to separate from normal water. Thus low abundance of heavy water coupled with a very poor separation factor make the heavy water production an extremely difficult task. Not only are the plants highly complex in their configuration, but are also highly energy intensive too. The specific energy consumption is 45 GJ/kg of D<sub>2</sub>O in case of H<sub>2</sub>S-H<sub>2</sub>O exchange process while it is 33 GJ/kg in case of NH<sub>3</sub>-H<sub>2</sub> exchange process. Even 1% reduction in specific energy consumption will result in annual saving of Rs.2.7 crore taking all the operating heavy water plants into account. Heavy water contributes to something between 15 to 30% towards cost of nuclear power generation- depending upon vintage of the plant. Considering the fact that energy constitutes 70% of the works cost of production of heavy water, energy conservation in HWPs was given top most importance.

The vast operating experience, subsequent improvements incorporated in the technology and various innovative strategies implemented have enhanced the production and resulted in reduced energy consumption.



The process simulation techniques employing rigorous mathematical modeling have yielded re-optimised process parameters which have resulted in more energy efficient operation of the Plants.

### **Front end Technology**

HWP-Baroda operating with feed synthesis gas from GSFC at 650 bar pressure had to suspend its operation since GSFC switched over to low pressure (120 bar) ammonia plant (Linde technology based on PSA SYSTEM). HWB had taken an advance action of developing the ammonia-water deuterium exchange process by setting up of a pilot plant at Baroda. With this the technology demonstration project at HWP Baroda is set up and is under commissioning. As the feed is water in place of synthesis gas, this plant is now independent of the fertiliser plant.

### **Ammonia Absorption Refrigeration (AAR) - Spin-Off Technology**

HWB has developed a novel AAR system capable of generation of refrigeration at  $-30^{\circ}\text{C}$  with improved coefficient of performance (COP). The improved AAR system is incorporated at HWP, Baroda and is under commissioning.

AAR system is also implemented at HWP, Tuticorin. It generates refrigeration at  $-25^{\circ}\text{C}$  &  $-11^{\circ}\text{C}$  and generated 300 Ton of refrigeration by 3.75 MT/hr of surplus steam. The system was commissioned in January 2004 and is running satisfactorily. The system is integrated with the existing vapour compression system. The Coefficient of Performance (COP) of the system is about 0.6 as against the last achieved in R&D facilities 0.52.

### **Sodium Technology**

Liquid metals, and among them liquid sodium, meets almost all the requirements of a fast reactor coolant with its high thermal conductivity, reasonable specific heat, low neutron moderation and absorption and high boiling point giving a large operating temperature range at near atmospheric pressure. High chemical activity of sodium including its violent reaction with water is a matter of concern in its large-scale handling. However, this is fully understood and the design of engineering systems takes care of this aspect. With several experimental and test facilities

established over the years in this country, 'sodium technology' has reached a level of maturity. The work on sodium was initiated in early 70's in a modest way. The programme initially focused on safe handling of liquid sodium in pumped engineering scale loops, reactor component tests, sodium instrumentation and, last but not the least, in preparing 150 tonnes of sodium coolant of reactor grade for Fast Breeder Test Reactor from commercially available grade. By 1985 when Fast Breeder Test Reactor attained criticality, the experimental sodium technology and engineering programme had matured enough to tackle future developments in support of the 500 MWe Prototype Fast Breeder Reactor (PFBR), the conceptual design of which had by then taken shape. Several small and medium size sodium loops were in operation for studies in liquid metal corrosion, liquid metal heat transfer and calibration of certain reactor instrumentation.

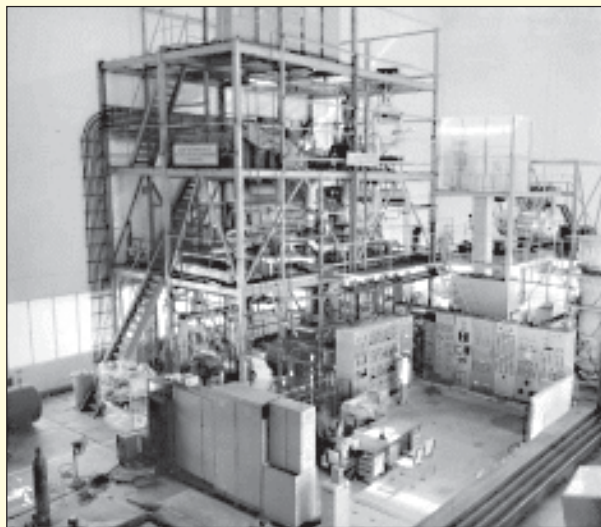
### **Experimental Facilities**

Considering the earlier requirements of FBTR and presently PFBR, many experimental sodium facilities have been constructed and operated at temperatures upto 873 K. Major facilities include Large Component Test Rig (LCTR) (a test facility with 80 t sodium hold up), Sodium – Water Reaction Test Facility, Steam Generator Test Facility (5.5 MWt), 500 kW Sodium Loop (a facility established during 1970s), etc Design, construction and operation of these facilities have given enough confidence in the design of heat transport systems for reactors and other facilities. Even though sodium has high boiling point, the vapours generated even at 823 K can cause problems in narrow crevices in the reactor systems. To study aspects such as heat transfer from hot sodium to the upper cover gas regions, temperature distribution in critical areas and convection currents in annular spaces in cover gas region of the reactor systems, elaborate experimental studies were carried out in LCTR. Also critical components of the reactor such as control and safety rod drive mechanism (CSRDM), diverse safety rod drive mechanism, fuel-handling equipments are tested at rated reactor environments before installing in the reactor system. The components have to qualify for the performance requirements in such testing process.

Special requirements are imposed on components such as cold trap (used for purification), sodium vapour trap etc. The



*Large component test rig*



*500 kW sodium loop*

secondary side of the reactor cold trap is loaded heavily by hydrogen and needs to be regenerated. Regeneration of the FBTR secondary cold trap was demonstrated. The cover gas argon carries a large amount of sodium vapour/mist along with that in flowing argon systems. This mist has to be separated using special techniques by condensation and filtration. Also in the regions above the free level of sodium in the reactor, large convection current takes place. This carries large sodium aerosols to the cooler regions at the top of the reactor and also causes temperature dissymmetry along the circumference in large diameter parts. To understand and to reduce / avoid the temperature difference experiments were carried out in large experimental facilities.



*Sodium test vessel for CSRDM*



*Sodium vapour deposition in cover gas region*

### **Sodium Purification**

Sodium is produced by Down's process which involves electrolysis of molten sodium chloride at 873 K. The major impurities present in commercial sodium are oxygen, calcium,



carbon and chlorine. Even though the pharmaceutical industries uses large quantities of sodium, they are in solid form with high impurity content. Since it is used in liquid form in the reactors, it has to be purified and maintained in pure state to reduce the corrosion of construction materials and to reduce the possibility of plugging of narrow passages in the system. The corrosion of structural materials (SS 304/316) in a pure system is less than 20 micron (mm) per year. The commercial grade sodium can be purified to the required purity by filtration in the first stage and by 'cold trapping' in the second stage. In the cold trapping process, the temperature of sodium is brought below the saturation temperature of impurities and the material is retained in a mesh filled vessel called 'cold trap'.

The purification of sodium to nuclear grade was demonstrated during 1975-78 and about 150 t of sodium was purified to nuclear grade and supplied in 1983-84 to Fast Breeder Test Reactor at Kalpakkam. Subsequently about 100 t



*First charging of commercial sodium brick for purification*

was purified for use in experimental facilities operating at high temperatures. The road map for processing 1750 t of sodium required for Prototype Fast Breeder Reactor has now been laid.

Besides purification, sampling, analysis and monitoring of impurities in sodium at ppm and ppb levels are developed. Flow through sampling technique and overflow sampling technique are deployed in all the facilities. In the later case, the entire



*Transport of purified sodium to FBTR in liquid condition*

quantity of sample in the crucible is taken for analysis, thus avoiding segregation of impurities. The analysis and monitoring of impurities involves off-line chemical analysis and on-line impurity monitoring. In off-line analysis, sodium samples are handled in high purity inert atmosphere glove boxes. After distillation of sodium, the impurities are analysed using absorption spectro-photometry or inductively coupled plasma mass spectrometry.

To monitor and to measure the concentration of impurities in sodium, many on-line instruments are developed and tested. All engineering systems usually have a device called plugging indicator, wherein the saturation temperature of impurities is monitored. This is a simple on line system that gives the gross concentration of impurities within an hour. The diffusion type (in sodium and cover gas) hydrogen meters (using the principle of diffusion of hydrogen through nickel to a high vacuum system) and electrochemical type meters were developed.

### **Sodium Pumps**

The reactor systems require a range of flow rates of sodium. For low flow rates, flat linear induction pumps, annular linear induction pumps, d.c. conduction pumps (immersible in sodium) and a.c. induction pumps are used. Many such pumps were designed (with the support of IIT-Madras) and fabricated indigenously. They were also tested in sodium facilities for performance. To meet the requirement of large flow rates in



*Centrifugal pump – model test facility*



*Centrifugal pump – rotor assembly test facility*

primary and secondary circuits of Prototype Fast Breeder Reactor, centrifugal pumps having flow rates of 4.13 m<sup>3</sup>/s and 3.34 m<sup>3</sup>/s were designed. The hydraulic design of these pumps posed a formidable challenge because of their large capacity to be delivered under modest net positive suction head (NPSH) coupled with the need to restrict their overall diameter, which in turn influenced the overall diameter of the reactor vessel. This implied that the pump would operate with cavitation to a small extent but again without producing significant erosion damage to the impeller. The design was developed in collaboration with an Indian Industry after a long drawn experimental programme on scale models. Similarly the manufacturing technology of pump components such as shaft, impeller, hydraulic bearings etc. was developed indigenously. All the sub-components such as long shaft have been tested for performance.

### **Material Corrosion**

The materials used in reactor systems such as stainless steel 304, 316, 304 LN, 316 LN, Modified 9 Cr 1 Mo etc. are exposed to sodium at different operating conditions and the effect on corrosion by leaching of constituent elements, mass transfer of interstitial elements like carbon etc. have been studied in experimental facilities. To study the carbon transfer and corrosion in stainless steel systems such as the primary circuit of fast reactors, a Mass Transfer Loop was operated for nearly 36,000 h with specimens at temperatures from 350 to 650 °C. Also to understand the behaviour of carbon in the secondary circuits of PFBR, wherein 316 LN and modified 9 Cr 1 Mo materials are involved, a Bi-Metallic Sodium Loop is in operation.

Based on the data generated in the last 30 years, the thickness loss is established to be less than a micron (micrometer) per year, which is considered negligible. However, a design allowance of 20 microns/year is considered to account for uncertainties on the sodium side.

To study the mechanical behaviour of PFBR component materials such as low cycle fatigue and crack growth and creep-rupture in the temperature range of 823 – 923 K, two sodium facilities were constructed and operated. The initial results from these tests are certifying the performance of indigenous materials for use in PFBR.



*Sodium-flow meters – permanent magnet type*



*Sodium level probes – resistance type*





Sodium fire

### Activity Transport

In a nuclear reactor, radionuclides are produced in the core region by neutron activation and fission. They are released slowly by corrosion and mass transfer processes and these deposit on other cooler regions. The breach of the clad of the fuel will lead to release of fission products in sodium. The release behaviour and deposition pattern are modelled using computer codes. They are also being studied in experimental sodium facilities. Some of these are trapped in cold trap. Radionuclide traps using reticulated vitreous carbon are deployed to trap  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ . Decontamination of radioactive construction materials using chemicals such as sulpho-Phosphoric acid solution has been studied and recommended for PFBR.

Metallic sodium has been used since the beginning of the 20<sup>th</sup> Century in chemical and pharmaceutical industry primarily as a reducing agent because of its chemical properties. However later years saw its applications growing as a heat transfer agent, thanks to its excellent physical properties, mainly high thermal conductivity coupled with low viscosity and low density. However, its potential was not exploited until the advent of fast (neutron) reactors where it has earned a place of honour

as a very effective coolant. Despite its high chemical reactivity, which is a strong disadvantage, it has been accepted universally as a fast reactor coolant due to its favourable nuclear properties and to a lot of work that went on in experimental and test facilities in several countries to muster what is called “sodium technology”. Today liquid sodium can be handled without difficulty and safely in engineering scale systems involving tonnes of quantities.

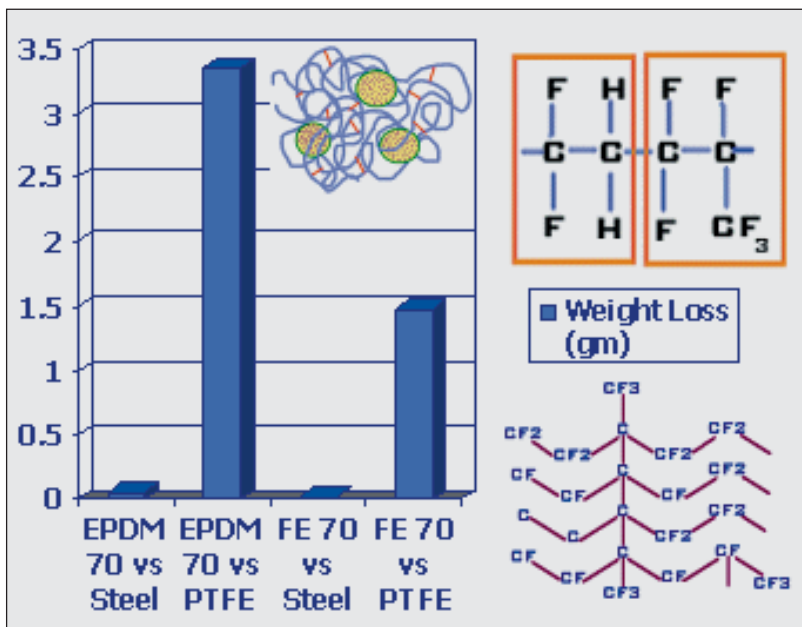
### Towards Reliable & Indigenous Polymer Materials for Applications in Nuclear Power Plants (NPP)

Organic materials can be of wide use in NPP as components and working fluids of safety significance. These include seals, bellows, gaskets, electrical insulation, gloves, booting, lubricants, hydraulic fluids, adhesives and coatings. Apart from lubricants and hydraulic fluids, all other components are made of polymers (thermoplastics, elastomer, thermosetting materials), a class of organic materials made of long-chain macromolecules. Design and production of polymer components do not follow the conventional route of handbook guidelines and closed-form-solutions because of issues like proprietary nature of material/manufacture information, large deformation and material nonlinearity.

This, coupled with the demands of reliability under uncommon/hostile environment, maintainability and lack of application-specific data from commercial manufacturers brings in the need of development effort backed by sound quality measures. Development and indigenization of Fast Breeder Reactor elastomer seals was an important step towards import substitution, self reliance and standardization of critical components made of organic polymers. Development of inflatable seals for PFBR and FBTR was taken up by IGCAR in collaboration with Defense Materials & Stores Research & Development Establishment (*DMSRDE*), Kanpur and ten other Indian Agencies (*including four IITs*).

This was the first such endeavor that had now set the foundation for materials, sizing, manufacture, adhesive, coating and quality standards for other polymer applications. Seals of ~0.5 m & ~1.5 m diameter have already been produced and the reactor sized seals (~6.3/4.2 m diameter for PFBR; ~3.5/2.5 m diameter seals for FBTR) are expected to be delivered by mid of 2005 after the validation of Plasma Teflon Anti-friction

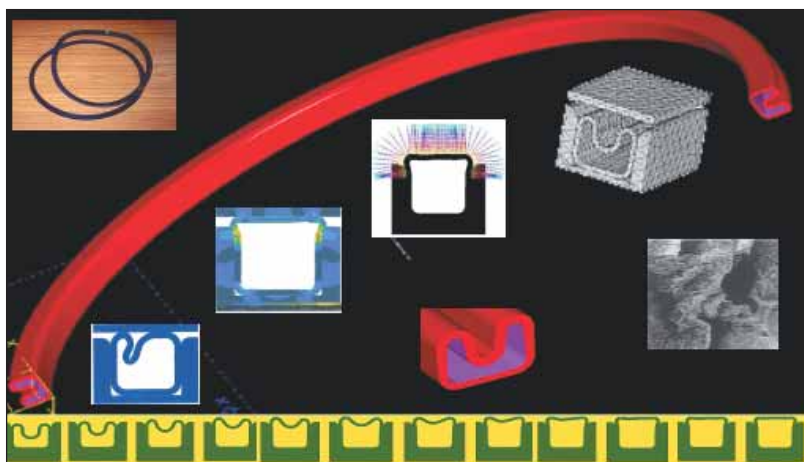




Comparative wear of EPDM & Fluorocarbon; **Insert** (clockwise):  
 i) Elastomer molecular architecture ii) Fluorocarbon chemical structure iii) Typical structure of PECVD Teflon Coating

coating on the seal rubbing face and after testing under simulated reactor conditions.

An Inflatable seal, a toroidal elastomeric membrane held in rectangular metallic (*carbon steel*) groove by adhesive and inflated by Argon gas acts as the primary and secondary barrier to radioactive gas leakage) in PFBR and FBTR rotatable plugs respectively. The PFBR seal has to function without failure for a minimum period of ten years under 393 K and a cumulative



3-D solid model of inflatable seal; **Insert**: Photograph of ~ 0.5 m diameter seals produced (top left corner);(clockwise from bottom left) Finite element models of i) Seal Failure ii) Stress Field in inflated seal iii) Contact pressure profile iv) 3-D seal-groove mesh; SEM image of surface degradation of Silicone after 2000 hours of exposure to sodium aerosol at 120°C. Bottom: Finite element simulation on progressive inflation of inflatable seals

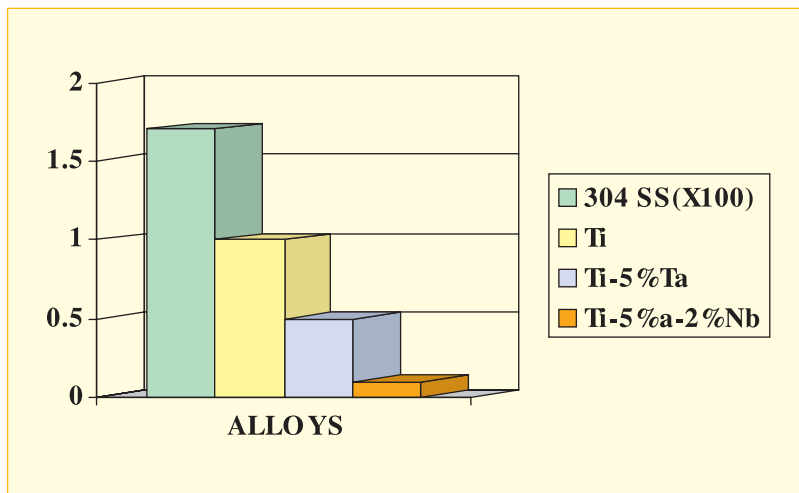
gamma dose of 2000 Sv in an atmosphere charged with Air, Ar, Sodium Aerosol, Kr, Xe and ozone. The seal, which remains engaged all the time, oscillates and rubs (*speed 75/2 mm/s*) after every ~ 8 months of static operation for ~20 days. Cumulative travel in ten years is 100 km. Out of the four candidate elastomers, fluorosilicone and silicone were eliminated because of bonding difficulties and Sodium Aerosol incompatibility. Based on further studies of several properties, EPDM & Fluorocarbon were selected for FBTR (*operating temperature: 323 K*) and PFBR respectively.

The spectrum and magnitude of operating conditions of PFBR inflatable seal suggest that Fluorocarbon could be adopted for all sealing applications of PFBR. The EPDM composition developed could be of similar use in Thermal Reactor Seals. The Plasma Enhanced Chemical Vapour Deposition (PECVD) Teflon anti-friction coating procedure being) for inflatable seal can be adopted for all fast reactor dynamic seals. This has now created the possibility of the simple and reliable “One material, one coating and one specification” approach for reactor seals which could be extended and standardized to a seal design code.

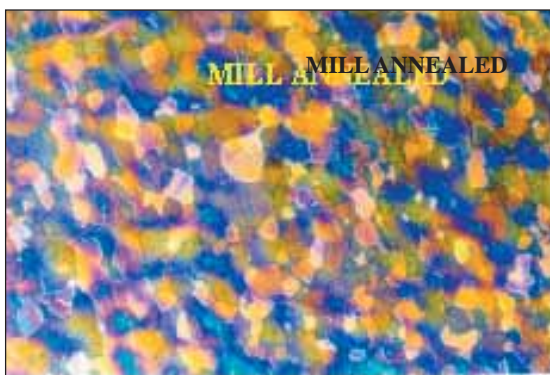
## REPROCESSING MATERIALS

### Development Of Materials For Dissolver Tank Assemblies of Fast Reactor Fuel Reprocessing Plant

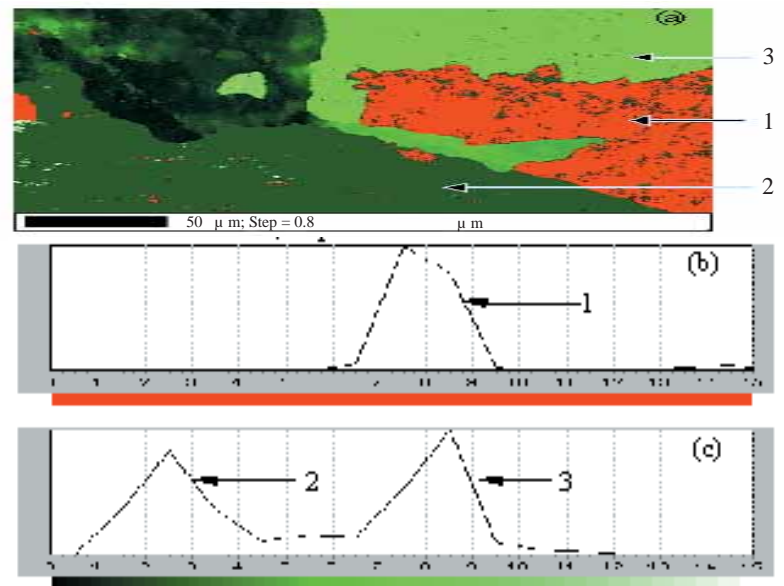
Demands on structural materials for reprocessing spent fuel of fast reactor assembly are stringent due to the high concentration of plutonium, which has forced the conventional PUREX process to be changed to electro-oxidative process. In this, the structural materials are exposed to high molality of boiling nitric acid, which is orders of magnitude more corrosive than the environment in PUREX process. Hence, replacement of conventional materials by more corrosion resistant materials would increase the lifetime of the component in addition to reducing radio-active waste. The corrosion rates of 304 L, pure Ti, Ti-5%Ta and Ti-5%Ta-2%Nb make them unacceptable. Hence, a Ti-5Ta-2Nb alloy was fabricated and examined for its fabricability, weldability, optimization of thermo-mechanical treatments and corrosion behaviour in boiling nitric acid. Fabrication of Ti based alloys is known to be easier in the duplex phase field of high temperature bcc  $\beta$  and low



Comparison of corrosion rates of different structural alloys for reprocessing applications. Corrosion rate of Ti-Ta-Nb is the least (0.1 mpy) against Ti-5%Ta (0.5 mpy), Ti (1 mpy) and Stainless



The thermo-mechanical treatments of the Ti-Ta-Nb alloy can yield either desirable (left micrograph) or deleterious structures, with corrosion rate in boiling HNO<sub>3</sub> as 0.3 and 1.5 mpy respectively



Orientation Imaging Microscopy of Ti-Ta-Nb alloy, showing the a lamellae in different colonies but with same orientation. Each colour denotes one particular orientation of the a lamellae, imaged using Electron Back Scatter Diffraction technique in Scanning Electron Microscope

corrosion rate is below 1 mpy (mills per year) in liquid and vapor state, while it is 2.5-3 mpy in condensate phase. These studies showed that this alloy exhibits a superior corrosion resistance as compared to the presently used SS 304 and Grade 2 Ti. The measured Yield strength and UTS are in the range of 300-340 MPa and 410-440 MPa respectively with 30-35% ductility, which are comparable to that of commercial Ti alloys. Weldability studies on 3mm plates of Ti-Ta-Nb alloys enabled selection of welding and weld qualification procedures. Since most of the failures in Ti alloys during service occurred in the weld, simulated weld and HAZ structures were studied in detail and a microstructural map was generated. This can be used to predict the microstructures that would result for various cooling rates.

### Mixed Oxide Coated Titanium Anodes (MOCTA) for Enhanced Life in Electrochemical Applications

Electrochemical methods are one of the more promising ways of dissolving and purifying the spent nuclear fuel from reactors compared to the conventional chemical methods. A number of electrochemical processes are currently employed world wide due to their simplicity, high efficiency and easy control over the process including remote operation. They are, electrolytic dissolution and conditioning, electrolytic partitioning and purification, electrolytic production of uranous ions,

temperature hcp  $\alpha$ . The transition temperatures of this alloy were evaluated using metallography, DSC and computational methods. The flow chart for the thermo-mechanical processing is also developed. Physical metallurgy data base for this alloy was established and the thermo-mechanical treatments yielding desirable and detrimental structures with respect to corrosion behaviour were identified. Controlled treatments were carried out based on experience of commercial  $\alpha+\beta$  Ti alloys to identify optimum microstructure for best performance. Evaluation of mechanical and corrosion properties show that the average

electrolytic destruction of organics, nitric acid and radioactive wastes etc. All the above processes use nitric acid of various concentrations, from room temperature to boiling conditions, and with the addition of redox systems for improving the current efficiency. The success and current efficiency of the electrochemical processes mainly depend on the durability or the corrosion resistance of electrodes, electrocatalytic activity or the low over voltage for the desired rate determining electrochemical reaction, and high conductivity facilitating operation of the electrolytic cells at high current densities. In addition, to avoid minimum interruption to the operation longer life is of paramount importance while choosing an electrode for the electrochemical processes. Currently platinum metallic electrodes are being used. Platinum undergoes corrosion at high current densities of operation in nitric acid medium at high temperatures. Moreover, platinum is expensive. All this necessitated development of economical platinised electrodes with corrosion resistant substrates providing high efficiency on par with platinum electrodes. For the same reasons Plasma Modified Mixed Oxide Coated Titanium Anodes (PMMOCTA) of long life were developed

Development of a compact, dense and crack-free mixed oxide coating of  $\text{RuO}_2\text{-TiO}_2$  on pretreated titanium using plasma process consisted of the following steps:

a) A thin film of ( $\approx$  20-100 nm) Rutile- $\text{TiO}_2$  was developed by a plasma process on the surface of pretreated titanium. This acted as a stable interface to improve adherence and conductivity of the  $\text{RuO}_2\text{-TiO}_2$  coating which is subsequently formed on this thin film.

b) Formation of  $\text{RuO}_2\text{-TiO}_2$  coating by application of chemicals from which these constituents are derived in suitable proportion for maintaining the right chemistry to achieve a final thickness of coating in the range 5-25 microns.

c) Consolidation of the coating by a final heat treatment in a reactive oxygen plasma in order to minimise the flaws and cracks developed in the MOCTA coating prepared by conventional method.

The PMMOCTA electrode thus developed showed a five-fold increase in life compared to conventional electrodes.

To further increase the life of the electrode coatings, a new approach was made to develop thermochemically glazed metallic coatings with an intermittent MOCTA layer on Ti

substrate. Metallic coatings of Pt and Pt-Ir were prepared by thermochemical glazing process on titanium substrates. Titanium substrates with single layer of  $\text{RuO}_2\text{-TiO}_2$ , applied with Pt and Pt-Ir chemical solutions, were heat treated in vacuum at different temperatures from 973 to 1473 K. It was found that the specimens prepared at 1373 K showed better electrochemical performance in comparison with Pt sheet electrodes. Life assessment of these electrodes in simulated reprocessing conditions showed excellent performance in comparison with conventional MOCTA electrodes. They continued to work up to 1840 hrs at an operating current density of 12.8 mA/cm<sup>2</sup> without any failure.

### Double Oxide Coating on Titanium for Reconditioning (DOCTOR)

The presence of iron higher than 0.05 wt% in titanium creates corrosion problems in both base and the welded regions due to segregation of iron and formation of iron-rich intermetallics. During qualification of the raw materials procured for fabrication of electrolytic dissolver, and the welding procedure to be adopted, the corrosion test results indicated that titanium showed unacceptable corrosion rates for both unwelded, and welded specimens. The high corrosion rates were attributed to the high iron content of titanium (0.05 to 0.1) which caused deleterious dissolution at the surface. If the iron content is limited to less than 0.04 wt% (the solubility limit of iron in titanium), this problem can be avoided. The crucial role played by iron in deciding the corrosion resistance in concentrated nitric acid at high temperature motivated development of a suitable surface modification procedure.

Electrochemical anodization is a unique way of forming a surface oxide layer that can distinctly enhance corrosion resistance of several metals and alloys. A surface modification technology that could increase considerably the corrosion resistance of titanium in both parent and welded condition, and which can be applied for the fabricated dissolver vessel was developed. The main points considered in this development are : (i) a method to dissolve iron particles segregated/enriched at the surface using chemical solutions by simple immersion method; (ii) application of nitric acid based solution containing redox ions that can enhance anodic oxidation for forming a stable oxide layer; (iii) further stabilisation and growth of oxide



layer in an alternate chemical solution; and finally, (iv) conditioning of the surface film. A major feature was providing in-situ surface treatment to the electrolytic dissolver already erected in the plant. Several chemical treatments were attempted for improving the corrosion resistance. After surface treatments, the specimens were tested as per ASTM A262 practice C test in boiling 11.5 N HNO<sub>3</sub> solution for five successive periods of 48 h. Surface treatment of the specimen by anodising for 24 h in a solution of nitric acid containing Ru, Cr and HF, and then subsequent anodic treatment in a solution of 10% ammonium persulfate followed by conditioning in hot water was found to result in reduction of corrosion rates to about 4 and 6 mpy (0.1 to 0.15 mm/year). This technology for developing a modified oxide layer was named as DOCTOR (Double Oxide Coating on Titanium for Reconditioning), and can be used for surface modification of dissolver made of titanium. After the DOCTOR coating, the surface developed a smooth appearance, and also exhibited higher polarization resistance confirming superior corrosion resistance. Development of this technique is a major step forward in the application of commercial grade titanium for manufacturing of dissolver vessels.

## ADVANCED MATERIALS

### Development of ZnO Varistor

ZnO varistor is a highly non-ohmic multiphase polycrystalline ceramic device, primarily composed of ZnO with other minor additive oxides. The varistor is usually made of zinc oxide (typically 80 - 90 %) and additives or dopants such as bismuth oxide, cobalt oxide, manganese oxide, chromium oxide etc. Additive oxides play vital role in the microstructural and electrical properties of zinc oxide varistors.

The excellent non-linear characteristics and surge protection capability of ZnO varistor has resulted in its extensive applications in electronic circuits and high voltage transmission systems. High voltage transmission systems demand varistor with high breakdown field. High breakdown field can be achieved with smaller grain size, which in turn calls for fine starting powders and/or sintering at lower temperature where grain growth is inhibited.

The main applications of ZnO varistors are in lightning arresters to protect electric power lines against lightning surges

and surge protection in relatively low voltage circuits. They are often called surge absorbers. The third application is voltage stabilisation, especially for high voltages above 10 kV and at low currents, less than 1 mA.

A process was developed for production of zinc oxide varistor powder directly from calcined zinc ore (sphalerite). The innovation relates to the process for preparation of zinc oxide based varistor in the form of a sintered body from calcined zinc ore by a chemical process to selective removal of impurities present in the calcine followed by addition of varistor constituent compounds in the solution stage to make up the varistor composition. The zinc oxide based varistor produced through this route exhibits high non-linearity index ( $\alpha$ , in the range of 25 – 45) and high breakdown field (4000 – 5000 V/cm).

A similar process has been developed for producing high purity ZnO powder from calcined zinc ore. The powder finds applications as starting material for preparation of various electronic ceramics. For these processes, two Indian patent applications have been filed.

### Development of Metal Bonded Diamond Scaife for Polishing Diamonds

The objective of this developmental work was to produce import substitute metal bonded diamond scaife to cater the need of Indian Diamond Industry. Metal bonded diamond scievers are used to polish gem grade diamonds. The technology for production of these scaives has now been standardized.. The scaives produced were field tested in several diamond cutting workshops in Surat. The performance characteristics were found to be equivalent to that of reputed imported ones in terms of cutting rate, surface finish, wear resistance of matrix and total working life. This development is significant considering the foreign exchange involved in importing these scaives by Indian Gem Industry. This development work was carried out under an MOU with a corporate body.

### Noble Metal Powders for Integrated Circuits and Multilayer Ceramic Capacitors

A very simple least energy intensive efficient low temperature chemical process for production of noble metal powder was developed. The process involves reduction of metal salts by polyol under atmospheric conditions at a temperature below

573 K. By using the process monodispersed spheroidal powders of copper, nickel and silver were prepared. The process can also be used for production of powders of other noble metals with controlled particle morphology. The copper powder produced is a potential candidate material for thick film conducting paste application. The morphology of the particles (narrow size distribution, spheroidal shape and fine size) along with purity of the powder produced by this process is ideally suitable for production of conductive paste for hybrid integrated circuit and for the metallization of multilayer ceramic capacitor (MLCC).

### High Purity Materials

The advent of nuclear technology and modern electronic industries in the country has brought in its wake the necessity to produce a wide range of metals and materials of exceptional high purity conforming to very rigid specifications. Production of high purity materials involves a variety of highly advanced technologies using specialized equipment. Anticipating this requirement, R & D work was initiated at BARC in the early sixties. Establishment of production level capabilities of the Special Materials Plant at NFC Hyderabad is the result of the dedicated efforts by many devoted scientists and engineers. This plant commenced regular production of high purity materials in the year 1972. Currently a variety of products are being prepared ranging from 6N purity metals like cadmium, tellurium, indium, mercury, antimony, gallium and metals like tantalum, niobium with its intermediates, magnesium granules, zirconium powder, zirconium-nickel alloy powder etc., to meet the indigenous requirements of the country. Development work was initiated to produce cadmium-tellurium and cadmium - sulphide compounds for making solar cells, C- 103 alloy, hydrogen - selenide gas, high purity tantalum pentoxide to meet the industries demands in the country.

The process technologies developed in the plant include : (a) Multi stage solvent extraction for separation and purification of tantalum & niobium from columbite – tantalite ore and tin slag, (b) Sodio-thermic reduction of potassium tantalum fluoride to produce tantalum powder and alumino-thermic reduction of niobium pentoxide to produce niobium metal, (c) Electron beam refining of tantalum, niobium metals and other special alloys, (d) Packed column fractional distillation of phosphorous oxy chloride boron tri-bromide, sodium iodide, antimony etc, (e)

Pyro-vacuum distillation of tellurium, cadmium, zinc, mercury etc., (f) Multi stage Zone refining of indium; tin, antimony, tellurium, cadmium etc., (g) Hydrogen embrittlement technique for producing zirconium titanium, high purity tantalum and niobium metal powders, (h) Rotating electrode process for producing high purity magnesium granules, (i) High temperature - high vacuum sintering, Annealing etc. For producing materials of very high purity, no single process is found adequate and hence a combination of the above techniques are often practiced to achieve the desired purity.

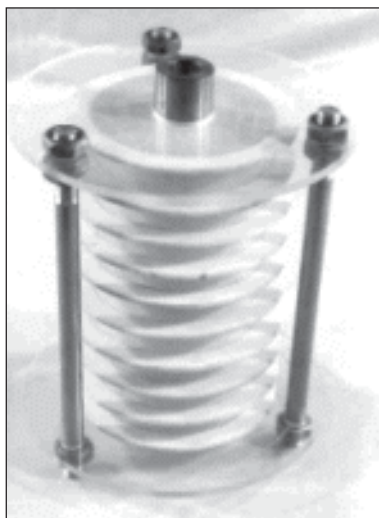
Having standardized the processes and having produced and supplied large quantities of special materials, the commercially viable technologies such as production of micron size zirconium metal powder, production of magnesium granules, production technologies of phosphorous oxy chloride, indium, sodium iodide, gold, silver and tantalum and purification of gallium metal have been transferred to private entrepreneurs on a “non-exclusive” basis. The plant is meeting the country’s requirements of high purity and specialty metals and alloys as well as many chemical compounds especially for the rapidly growing Electronics Industry.

### Development of Advanced Ceramics

Over the past three decades, significant developments have taken place in the field of ceramic materials resulting in proliferation of their applications in almost all the advanced fields like electronics, telecommunication, energy conversion and conservation, nuclear energy, space technology, biotechnology and a host of other engineering applications. While the work on ceramics activities started with the fabrication of ceramic nuclear fuel material in the early sixties, it is in the last two decades that a comprehensive programme on development of advanced ceramic materials for several structural, electronic and biomedical applications has been vigorously pursued in DAE.

### Alumina Ceramics

During the course of R&D work on alumina ceramics, processes were developed to fabricate impervious high alumina bodies (~94%  $Al_2O_3$  content) by using additives like clay and barium carbonate etc. High density alumina substrates (25x25x1mm) and translucent recrystallised alumina components were fabricated by using technical grade alumina



Capacitor bank assembly using electronic grade alumina components

(~99% purity) with appropriate MgO doping. High purity alumina powders were also synthesised by sol-gel process. Alumina components for dielectric applications have also been fabricated.

Marked improvement in mechanical properties was achieved by incorporating ZrO<sub>2</sub> dispersions (ZTA or zirconia toughened alumina ceramics) in alumina matrix. Apart from the conventional route of mechanical mixing of matrix and

reinforcement phases, new approaches on in-situ reaction synthesis of ceramic matrix composites like directed metal oxidation (DIMOX) have been developed. In this process, conventional fabrication techniques such as slip casting, cold pressing and injection moulding were used to form the final component shape. The preform is placed in contact with molten aluminium alloy in an oxidizing atmosphere. The composite reaction product mass grows through the preform infiltrating the reinforcement without displacing it. The process thus yields a fully densified net-shaped composite obviating the problems of shrinkage typically associated with the densification of ceramics.

Excellent chemical stability of alumina is very useful in corrosive atmospheres. Technology to fabricate extremely low leak rate alumina ceramics – to – metal seals using Moly-Manganese process was developed. In this method, precursor moly-manganese paste is applied to the recrystallised alumina and a suitable heat treatment is carried out. A nickel coating is then provided over Mo-Mn layer. Stainless steel members are then brazed to Nickel. All the process parameters were optimized and the seals were tested. Helium leak rate <math><10^{-9}</math> c.c/sec have been obtained. These feedthroughs have been used in critical applications.

### Development of Zirconia Based Ceramics

Materials from ZrO<sub>2</sub> with improved mechanical properties like partially stabilized zirconia (PSZ), tetragonal zirconia polycrystals (TZP), and the various possible systems of zirconia

toughened ceramics (ZTC) exploit the phenomenon of martensitic t@m (tetragonal to monoclinic) transformation of ZrO<sub>2</sub> to evolve super-strong ceramics. A range of structure – property-correlation studies were carried out with different variants of PSZ, viz. (i)Mg-PSZ (ZrO<sub>2</sub>-9.0 mol% MgO), (ii)Y-TZP (ZrO<sub>2</sub>-3.0 mol%Y<sub>2</sub>O<sub>3</sub>); of ZrO<sub>2</sub> bearing ceramic – ceramic composites, viz. (a) Zirconia Toughened Alumina, ZTA (containing upto 20 vol% ZrO<sub>2</sub>) (b)Alumina dispersed 3Y-TZP (particulate reinforcement upto 20 vol%).

Apart from the projected advanced engineering applications, zirconia ceramics are used as refractories and other special purpose products. For such applications the lime stabilized (fully cubic phase) form of ZrO<sub>2</sub> meets the requirements. Employing commercially available powders, fabrication of boats, crucibles, etc. was undertaken on a regular basis.

Material	K <sub>IC</sub> (MPa ÷ m)
Mg-PSZ	5.02
3Y-TZP	5.69
ZTA	6.22
3Y-TZP / Al <sub>2</sub> O <sub>3</sub>	8.00

Typical values of fracture toughness K<sub>IC</sub> obtained for various zirconia ceramics (Vickers indentation, 100N, 15 s)

Yttria stabilized cubic zirconia (Y-FSZ) has also found wide range of applications like solid electrolytes, oxygen sensors, thermal barrier coating etc. The mechanical and physical properties of zirconia based system are fine tuned by controlling the microstructure. Ideally nano crystalline powders offer the potential for improved process control. The hydroxide co-precipitation process is one of the most simple and cost effective method to prepare nano size powder. But the difficulty to exploit the full benefit of nanocrystalline size is the formation of agglomerates. A modified flow-sheet was developed to prepare a nano size Y-FSZ powder through co-precipitation method in the presence of poly ethylene glycol (PEG) and sulphate ion by reverse strike method. Nanocrystallinity of the calcined powder was established from X-Ray line broadening, specific surface area measurement and from TEM images. Sintering study confirms higher sinteractivity of the powder compared to conventionally prepared YSZ.



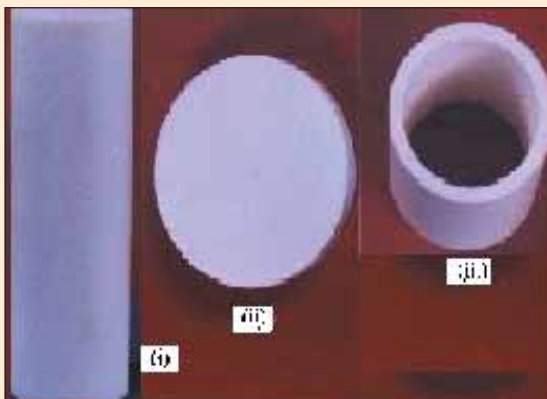
## Glass-Ceramics

Magnesium-aluminum-silicate (MAS) is an advanced ceramic having high thermal stability, very high electrical insulation, and is UHV compatible. In addition, it has good mechanical strength and can be machined to precise dimensions and surface finish with conventional carbide tipped tools.

It is available in the form solid discs (70mm dia x 25 mm height), solid rods (40mm dia x 100 mm height) and hollow cylinders (60mm OD x 45 mm ID x 90 mm height). They are also available as lugs /spacer rings, spacers, nuts and bolts.



MAS glass-ceramics in different sizes along with components.



## Combustion Synthesis of Ceramic Oxides in Batch Process

Combustion synthesis of fine ceramic oxides is generally conducted employing nitrate as oxidizer and citric acid, urea or glycine etc. as fuel. The exothermic reaction depends on the oxidant to fuel ratio used in the synthesis, combined with fire/flame, poses problems in bulk synthesis of ceramics. Significant progress was made in the preparation of a series of single and multi-component ceramic oxides in bulk quantities by batch process. The ceramic oxides produced include: ultra-fine ceria

for high end polishing of optical glass, and mono-phase lanthanum strontium manganite (LSM) and lanthanum magnesium chromate used as cathode and interconnect materials for Solid Oxide Fuel Cell (SOFC) respectively. A stainless steel reactor was designed, fabricated and successfully used to prepare these oxides in batch size of 250 g. Two patent applications have been filed, one for the design of the combustion synthesis reactor and other for the preparation of nano size ceria powder (for ultra fine polishing of optical glass) using this reactor

## Microwave Processing of Ceramics

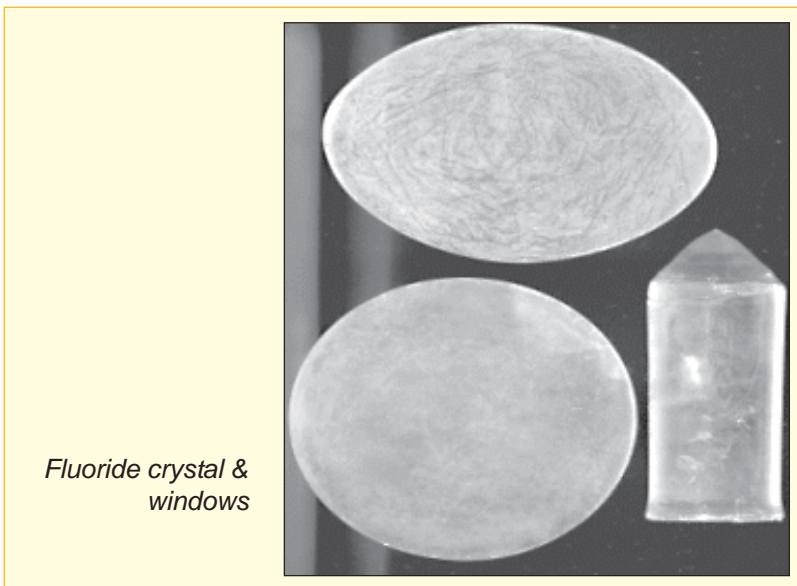
Detailed investigations were undertaken towards harnessing the phenomenon of microwave heating for the synthesis and processing of ceramic materials like  $ZrO_2$ , ZTA,  $Al_2O_3 - SiC$  composites, HTSC, etc. For synthesis routes like solution based homogeneous precipitation or solid state reaction in  $Li_2O - Ta_2O_5$  system, an enhancement in reaction kinetics was achieved. Sintering assembly was constructed by modifying 900 watt, 2.45 GHz microwave oven. To initiate heating, a hybrid mode was adopted using a thin layer of SiC powder as a susceptor. A shielded R-type thermocouple was used for sensing the temperature. Samples of 9Y-CSZ and 3Y-TZP were sintered at 1898 K and 1623 K respectively in microwave furnace where as to achieve comparable density by conventional heating, temperature in the range of 1923 K and 1673 K are required respectively.

## NON-OXIDE CERAMICS

### Transmitting Window Materials

BARC has been continuously developing single crystal transmitting windows of different alkali halides and alkaline earth fluorides. The entire spectral range starting from vacuum ultra violet to far infrared region can be covered by the set of crystals available. The technology for growth of crystals up to 50 mm diameter by Bridgman technique has been perfected to the level of batch production.

These are available as finished crystal windows of the sizes 25 mm, 37 mm and 50 mm diameter and are under regular production and being regularly supplied to various users all over the country.



### Silicon Carbide Ceramics for Structural and Tribological Applications

Silicon carbide is amongst the most important non-oxide ceramics for high temperature structural applications. Being a covalently bonded solid, it cannot be sintered to high density by conventional means. An extensive study on densification of silicon carbide in the presence of various additive combinations was carried out. Typically a fine powder of  $\beta$ -SiC (0.5  $\mu\text{m}$ ) along with the additives (Al, B and C) were subjected to hot pressing in the temperature range of 1973–2173 K. Fully dense (bulk density 3.18  $\text{g}\cdot\text{cm}^{-3}$ ) SiC samples were obtained after hot pressing at 2173 K.

### TiB<sub>2</sub>

Carbothermic reduction process was followed to produce TiB<sub>2</sub> from TiO<sub>2</sub> using B<sub>4</sub>C and carbon as reductant in the temperature of 1673 K and above. This material was hot-pressed to required density with and without the presence of MoSi<sub>2</sub> sintering additive.

### Bioceramics for Reconstructive Orthopaedic Surgery

Hydroxylapatite (HA) based ceramics have considerable potential in the field of prosthetic implants. The compatibility of HA, being the principal inorganic component of human bone and teeth, with human system is the main reason for its projected use in bio-implants. The synthesis protocol for reproducible grade HA powders was optimized. The powders were characterized through PSD (particle size distribution), chemical composition and XRD. Porous components using pure HA and HA-bTCP composites were fabricated and characterized for their microstructure and porosity. Currently, techniques for producing stable HA coating on titanium and titanium based implants are being explored.

The use of calcium sulphate based ceramics as a bio-active bone void filler is attracting considerable attention recently. It is realized that the quality of calcium sulphate and its physical characteristics like the size and shape of calcium sulphate are the key factors for its reproducible performance because these factors control the resorbing of the material in the human body at a rate consistent with new bone growth. Currently “Osteoset” material approved by US FDA is being used in the country for such applications. Experimental studies were, therefore,

Materials	Range (mm)
NaCl	0.2-15
KCl	0.21-20
KBr	0.23-25
LiF	0.12- 6
BaF <sub>2</sub>	0.15-12.5
CaF <sub>2</sub>	0.13-10

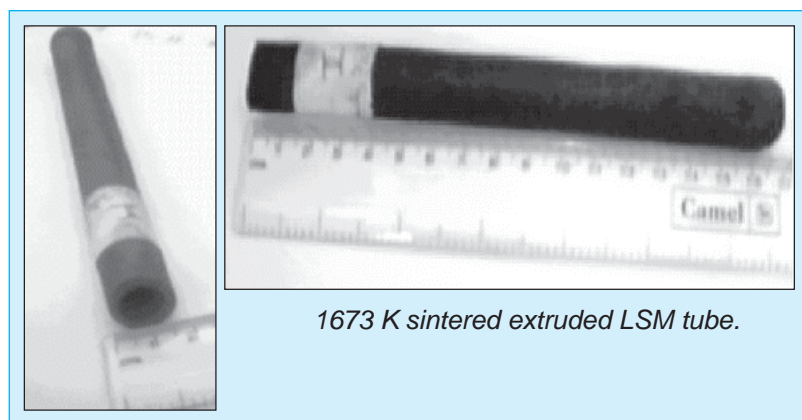
conducted to synthesize pure  $\text{CaSO}_4$  for use as a bone void filler, particularly a-hemihydrate through dehydration process using dilute  $\text{H}_2\text{SO}_4$ . Compacts having porosity and microstructure very nearly akin to "Osteoset" were fabricated and supplied to Tata Memorial Hospital and Sion Hospital, Mumbai for testing. Initial trials at Sion hospital have met with considerable success.

### Relaxor Ferroelectrics

Lead magnesium niobate (PMN) and lead iron niobate (PFN) are ferroelectric ceramics with interesting dielectric properties. Both of these ceramics exhibit broad and very large dielectric maxima ( $K=10000-20000$ ) and therefore are being used as raw materials for multilayered ceramic capacitors (MLCC). PMN also has a very high electrostrictive coefficient and therefore is suitable for making electrostrictive actuators. PMN and PFN were prepared by the conventional solid-state route as well as by a new semi-wet hydroxide route. These were consolidated by sintering in  $\text{PbO}$  atmosphere as well as by hot pressing. These were characterized for their physical, microstructural and dielectric properties. The semi-wet hydroxide route yielded product with considerably improved properties.

### Development of LSM Support Tubes for SOFC Cathodes

Solid oxide fuel cell is an emerging field for high temperature energy conversion technology. Though, various geometries have been proposed, a tubular geometry is being considered as a viable proposition. Co-precipitation method was adopted



for the preparation of LSM powder ( $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{2.93}$ ). In this method, mixed nitrate solution of La, Mn, and Sr ions are added in a precipitating bath at pH 8.0 in the presence of carbonate

ions. Powder calcined at 1273 K and above was characterized by X-ray diffraction technique to confirm the phase purity of the material.

Densification studies on powders with different concentration of poreformer were performed. Electrical conductivity and thermal expansion coefficient for this material were also determined. Conditions for shape fabrication by slip casting as well as extrusion were also optimized.

### Superconducting Materials and Applications

Apart from fuel fabrication, development and fabrication of Nb-Ti composite superconducting wire was initiated in 1982 at Atomic Fuels Division (AFD), BARC. Presently, 3 km single lengths of 1.3mm dia wire containing ~500 Nb-Ti filaments each of 40 $\mu\text{m}$  size with Cu:SC ratio of 1.15:1 are being produced successfully. A facility for continuous soldering of superconducting wire on to U-grooved rectangular OFHC copper channel has also been set up. On-line ultrasonic testing system has been incorporated to check the bond integrity of the cable. About 1 km single length soldered conductor has been produced and also tested at VECC, Kolkata. This conductor is comparable to the IGC, USA make conductor from UT point of view. The conductor will be suitable for cyclotron magnets. LTSC wires and cables will be suitable for various applications in frontier areas such as accelerators, fusion reactors, magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR), Superconducting magnetic energy storage system, MHD generators, magnetic ore separator, DC and AC superconducting motors, transportation and accelerator driven energy system.

Initial efforts in this field was towards reproducing results of observation of high temperature superconductivity in Y-Ba-Cu-O and related systems. With some optimization, superconductivity with transition temperature,  $T_c$ , above liquid nitrogen temperature could be routinely obtained. Similarly, when Bi based superconductors were discovered, the results on them were immediately reproduced and extended further.

Studies were also conducted on the synthesis of new materials with substitution of rare earth samples to see whether the superconducting transition temperature could be enhanced in these systems. The presence of mixed-valent copper and the nearly two-dimensional character of the  $\text{K}_2\text{NiF}_4$  structure are considered important for the occurrence of superconductivity





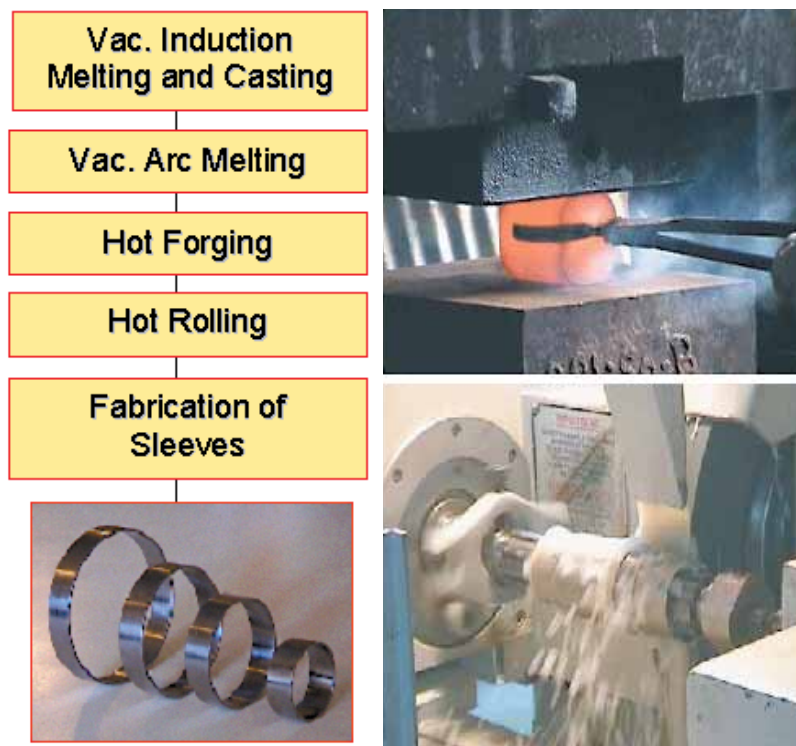
in  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  ( $T_c$  onset 36K). The effect of partial replacement of mixed-valent Cu by monovalent Ag on the superconductivity of this system was studied by varying the compositions  $\text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_{1-x}\text{Ag}_x\text{O}_4$  (0.0 ≤ x ≤ 0.15). All these compositions showed the tetragonal  $\text{K}_2\text{NiF}_4$ -type structure. In spite of the charge imbalance caused by Ag substitution, the  $T_c$  was found to decrease rather gradually from 36K for x=0.0 to 20K for x=0.15.

### Shape Memory Alloys

One amazing material in the group of advanced and smart materials is the shape memory alloy. A deformed and distorted object made from this alloy recovers its original shape and dimensions, when the temperature is raised. The shape memory alloy usually memorizes only the shape of the object at the higher temperature (the “recovered” shape) and, when “trained”, can also memorize the shape to be attained at the lower temperature (the “deformed” shape). This natural tendency of the shape memory alloys is derived from the reversible diffusionless (“martensite” phase transformation) manner in which the crystal structures change on heating or cooling past the characteristic recovery temperature. Of a reasonably large number of alloys in which this tendency (the “shape memory effect”) has been discovered, the Ni-Ti based alloys are the best in terms of shape memory properties and their viable engineering applications. At this time, a very wide gamut of medical, engineering, nuclear and space applications are made that successfully exploit the excellent biocompatibility, superelasticity, shape memory, damping characteristics and the large recovery strain and stress of the Ni-Ti based shape memory alloys. However, these alloys are expensive and relatively difficult to prepare and fabricate. On the other hand, though the Cu-based and

the Fe-based shape memory alloys are inferior to the Ni-Ti alloys, they are easier to fabricate and much cheaper.

Research on shape memory alloys has been pursued for nearly two decades in DAE, from which a number of important scientific contributions on material characterization and phase transformations related to the shape memory phenomena have originated. These include rationalization of reversion stress, crystallography of the martensitic transformation, the nature of self-accommodation of martensite crystals and the crystallographic interrelations between the shape memory effect and martensitic microstructure. The melting and fabrication routes



Flow sheet for heat shrinkable Ni-Ti-Fe shape memory alloy sleeves developed at BARC

The hot forging of Ni-Ti alloy ingots and the machining of heat shrinkable sleeves from electric discharge machined blanks

for several shape memory alloys have been established and several Ni-Ti, Cu-Zn-Al and Fe-based alloys have been successfully produced. These efforts culminated in developing Ni-Ti-Fe shape memory alloys and heat shrinkable sleeves for the Light Combat Aircraft (LCA), neither of which is available for the defense and nuclear industry due to import restrictions. The entire flow sheet for fabrication of Ni-Ti-Fe sleeves for the LCA involving alloy preparation, fabrication and machining was

developed in DAE and scaled up to regular production level. An important requirement for developing applications of shape memory alloys is the necessary engineering design basis. An attempt in this direction has been the successful development of a mathematical model for the thermo-mechanical behaviour of this alloy. This model can be integrated with a finite element solver for developing the prototypes of simple applications.

The story of “Ore to Core - Competence In Materials

Technology” is in many ways typical of the deep reservoir of expertise developed by DAE. This is indeed one of the contributing reasons for its success independent of the external conditions of technology denial. In developing technologies for materials preparation to large scale industry development, equipment design to component manufacture, from technology transfer to development of support industries, DAE has not only become self-reliant but has also spawned many spin-offs to the Indian industry.



*The Ni-Ti-Fe heat shrinkable sleeves developed by BARC are used as fasteners in the Light Combat Aircraft under development at Aeronautical Development Agency, Bangalore. These sleeves have been tested and certified for airworthiness and application in combat aircrafts*

